* NOTICES *

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2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to a high molecular compound and its manufacturing method.

[0002]

[Description of the Prior Art]

Unlike it of low molecular weight, it is meltable to a solvent and the luminescent material and charge transporting material of the amount of polymers are variously examined from the ability of the organic layer in a light emitting device to be formed by the applying method. As a high molecular compound which can be used for electronic devices, such as polymers LED, as a luminescent material or a charge transporting material, what has phenylenevinylene structure, fluorene structure, phenylene structure, and poly thiophene structure is publicly known as a repeating unit. .

[0003]

[Problem(s) to be Solved by the Invention]

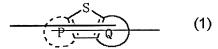
The purpose of this invention is to provide the polymers light emitting device (polymers LED) using a new high molecular compound useful as a luminescent material, a charge transporting material, etc., its manufacturing method, and this high molecular compound. [0004]

[Means for Solving the Problem]

A high molecular compound which has the structure to which one piece or two aromatic rings condensed the ring to a thiophene ring as a repeating unit found out that it was useful as a luminescent material, a charge transporting material, etc., and this invention persons completed this invention, as a result of inquiring wholeheartedly that an aforementioned problem should be solved.

[0005]

That is, as for this invention, a repeating unit is a following formula (1).



[Among a formula, although a P loop and Q ring show an aromatic ring independently, respectively, even if a P loop exists, it is not necessary to carry out it. Two joint hands exist on a thiophene ring and/or Q ring, respectively, when it exists on a P loop and/or Q ring, respectively when a P loop exists, and a P loop does not exist. On an aromatic ring and/or a thiophene ring, an alkyl group, an alkoxy group, An alkylthio group, an aryl group, an aryloxy group, an arylthio group, An arylated alkyl group, an aryl alkoxy group, an aryl alkylthio group, An aryl alkenyl group, an aryl alkynyl group, an amino group, a substituted amino group, It may have a substituent chosen from a group which consists of a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a

univalent heterocycle group, a carboxyl group, a substitution carboxyl group, and a cyano group.]

It comes out and a number average molecular weight of polystyrene conversion is related with a high molecular compound which are 10 3 – 10 8 including structure shown.

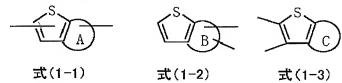
Structure shown by the above-mentioned formula (1) may be hereafter called thiophene condensed ring structure. A repeating unit including structure shown by the above-mentioned formula (1) may be called thiophene condensed ring unit.

[0006]

[Embodiment of the Invention]

As the high molecular compound of this invention,

the structure shown by a formula (1) -- a following formula (1-1) and (1-2) -- or (1-3)



[A ring, B ring, and C ring show an aromatic ring independently among a formula, respectively. These repeating units An alkyl group, an alkoxy group, an alkylthio group, An aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, An aryl alkoxy group, an aryl alkylthio group, an aryl alkenyl group, An aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, It may have a substituent chosen from the group which consists of a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, and a cyano group.]

It comes out and is a certain high molecular compound.;

[0007]

the structure shown by a formula (1) -- a following formula (1-4) -- or (1-5)



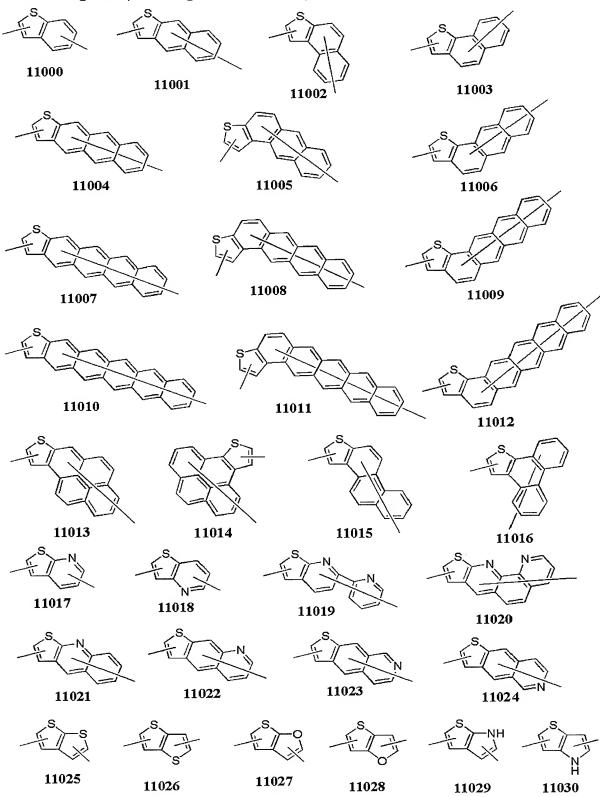
[D ring, E ring, F ring, and G ring show an aromatic ring independently among a formula, respectively. These repeating units An alkyl group, an alkoxy group, an alkylthio group, An aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, An aryl alkoxy group, an aryl alkylthio group, an aryl alkenyl group, An aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, It may have a substituent chosen from the group which consists of a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, and a cyano group.]

It comes out and the high molecular compound which is the structure shown is raised. [0008]

A P loop, Q ring, A ring, B ring, C ring, D ring, E ring, F ring, and G ring show an aromatic ring independently, respectively among the above-mentioned formula (1), (1-1), (1-2), (1-3), (1-4), or (1-5) a formula. As this aromatic ring, the benzene ring, a naphthalene ring, an anthracene ring, a tetracene ring, Aromatic hydrocarbon rings of a pentacene ring, a pyrene ring, a phenanthrene ring, etc.; complex aromatic rings, such as a pyridine ring, a bipyridine ring, a phenanthroline ring, a quinoline ring, an isoquinoline ring, a thiophene ring, a furan ring, and a pyrrole ring, are mentioned.

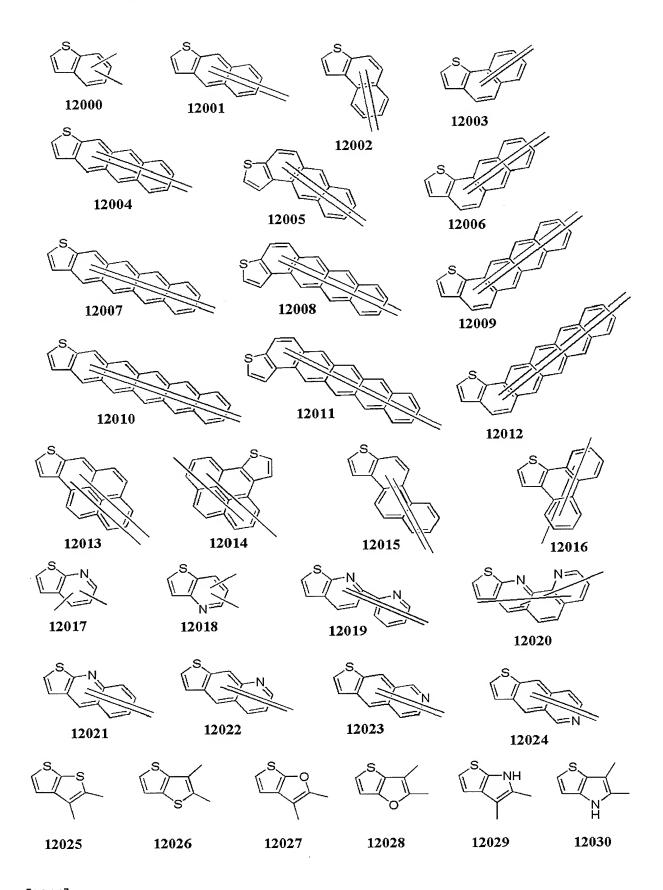
[0009]

The following examples are given as an example of a formula (1-1).

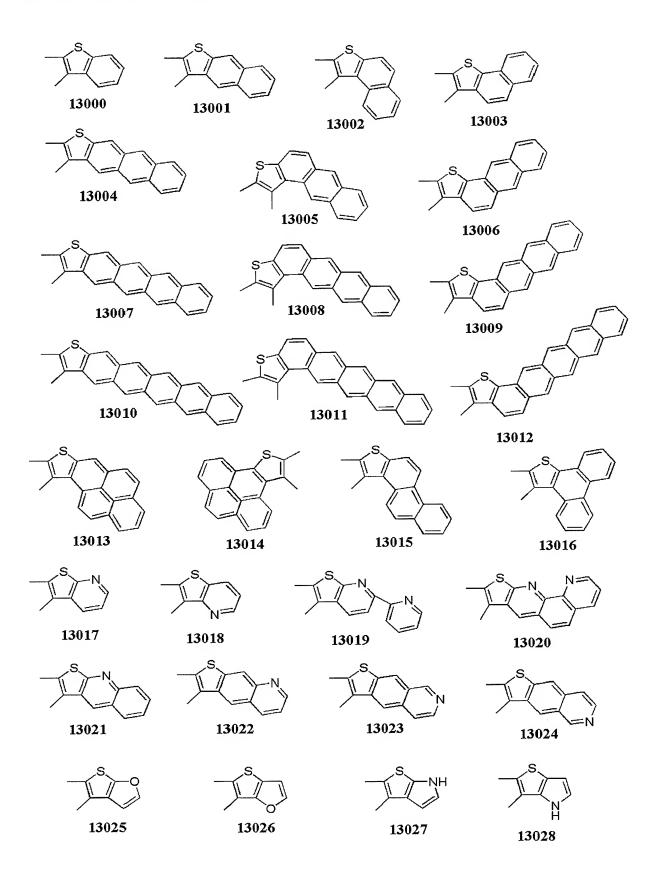


[0010]

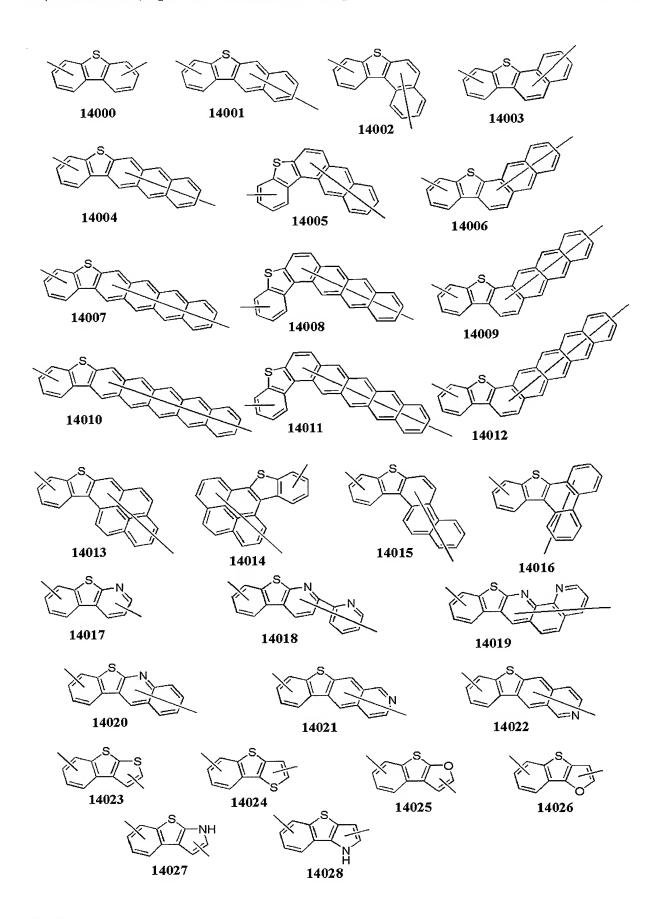
The following examples are given as an example of a formula (1-2).



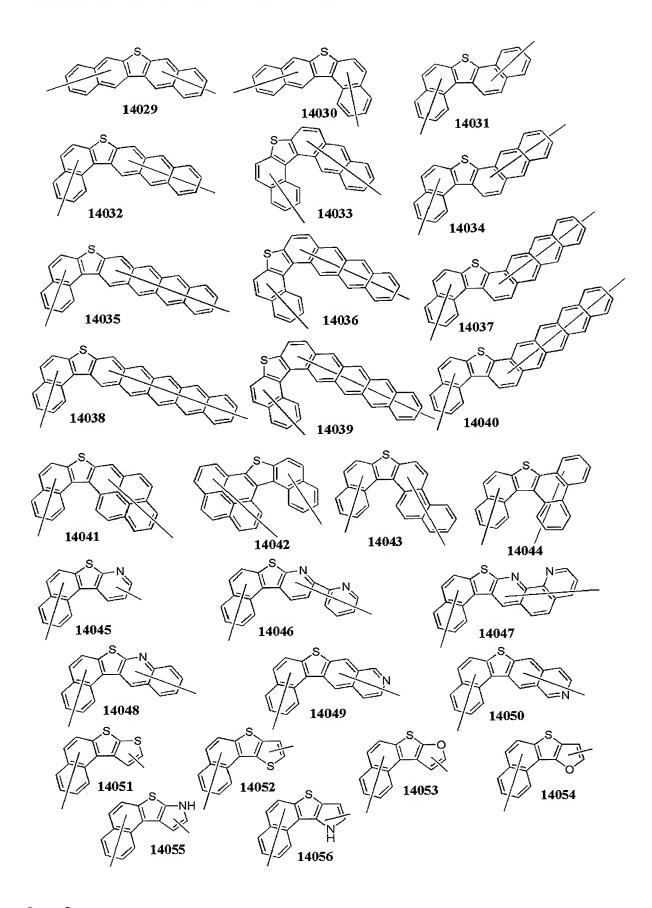
[0011] The following examples are given as an example of a formula (1-3).



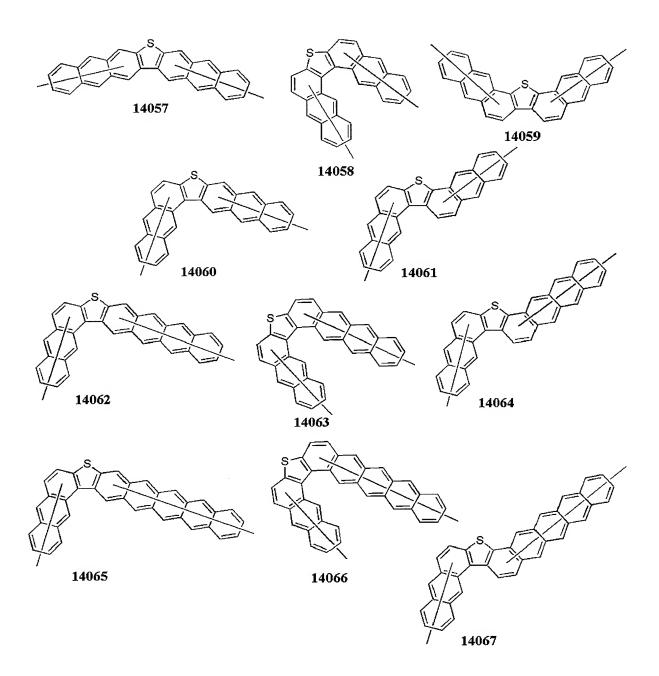
[0012] The following examples are given as an example of a formula (1-4).



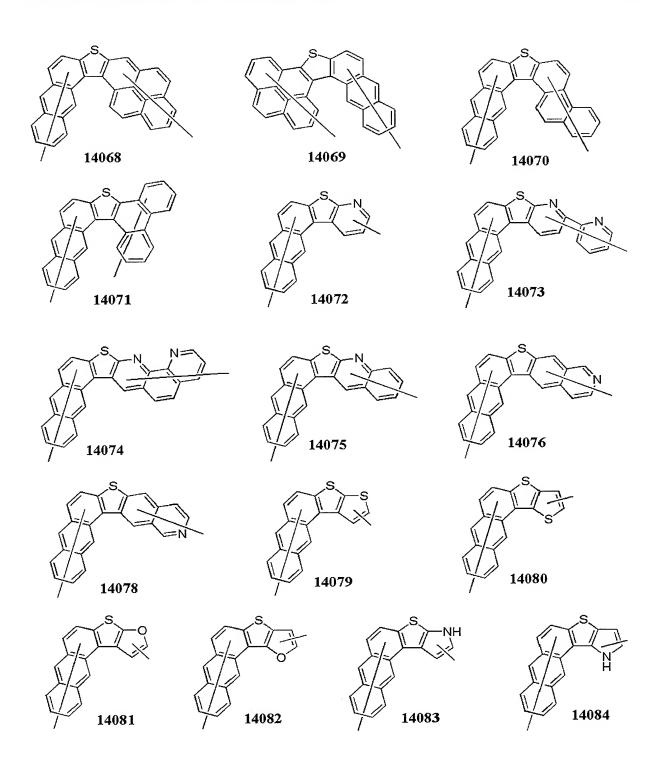
[0013]



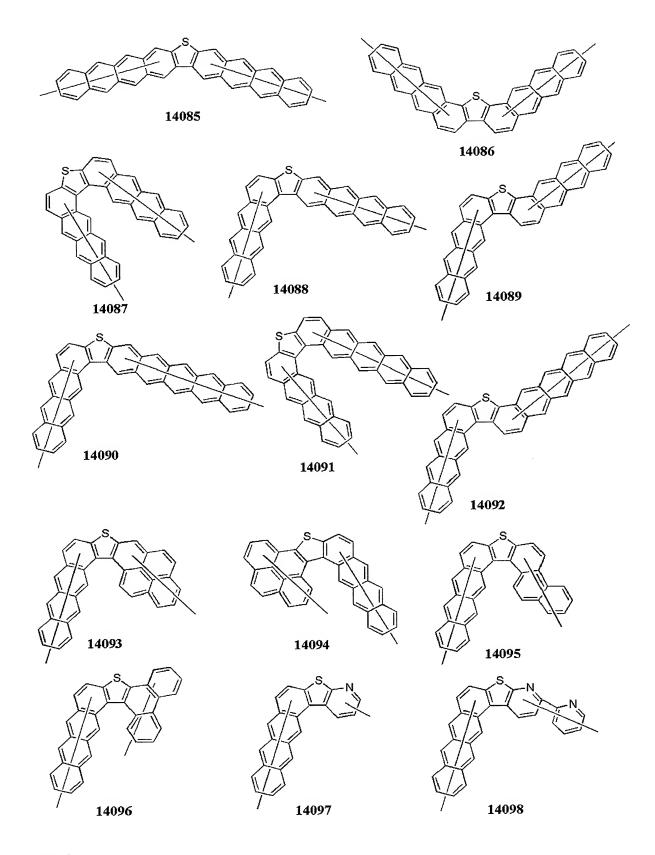
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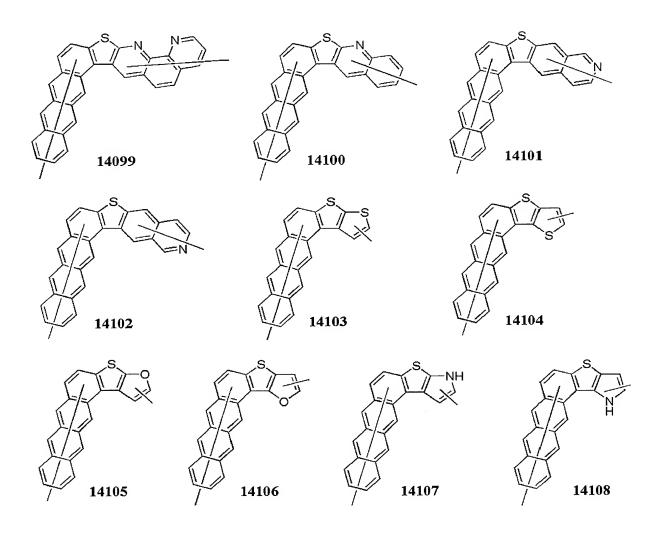
[0015]



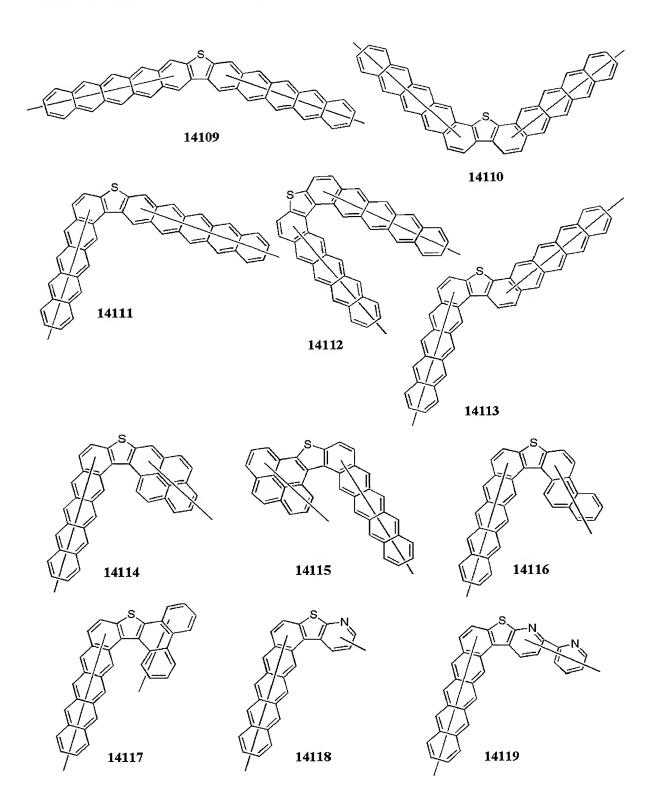
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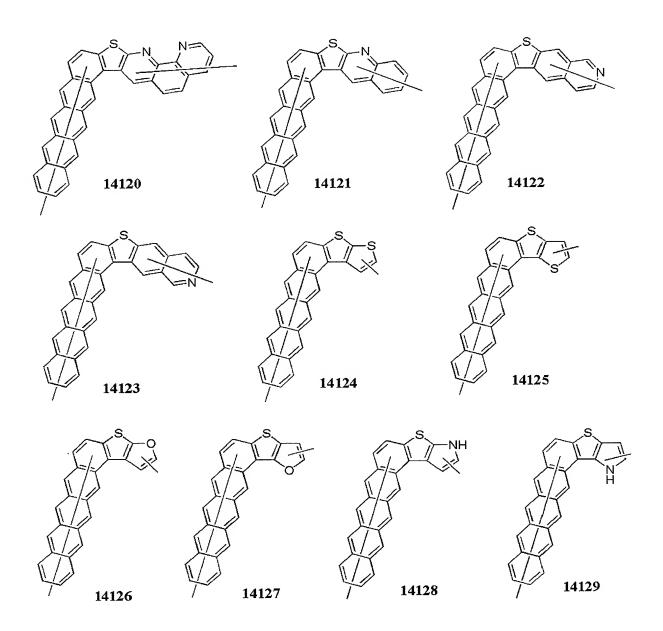
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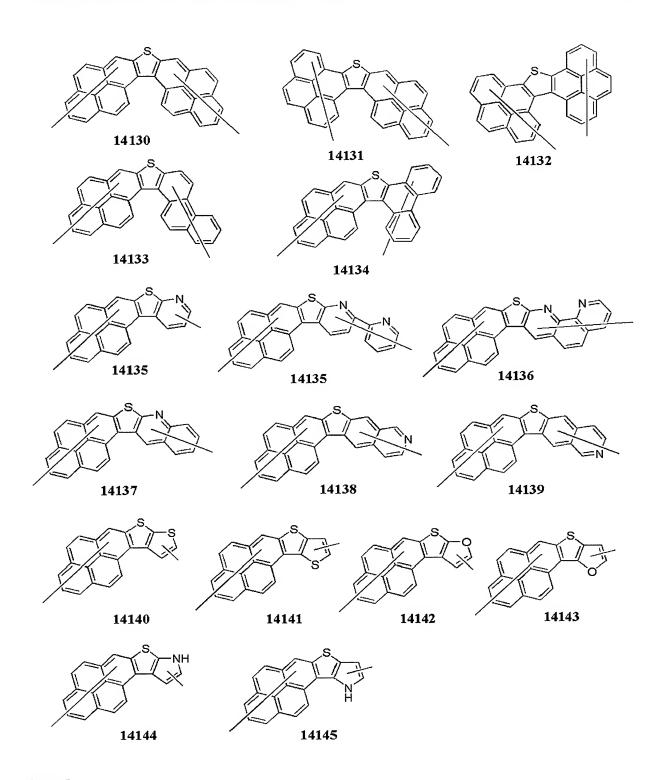
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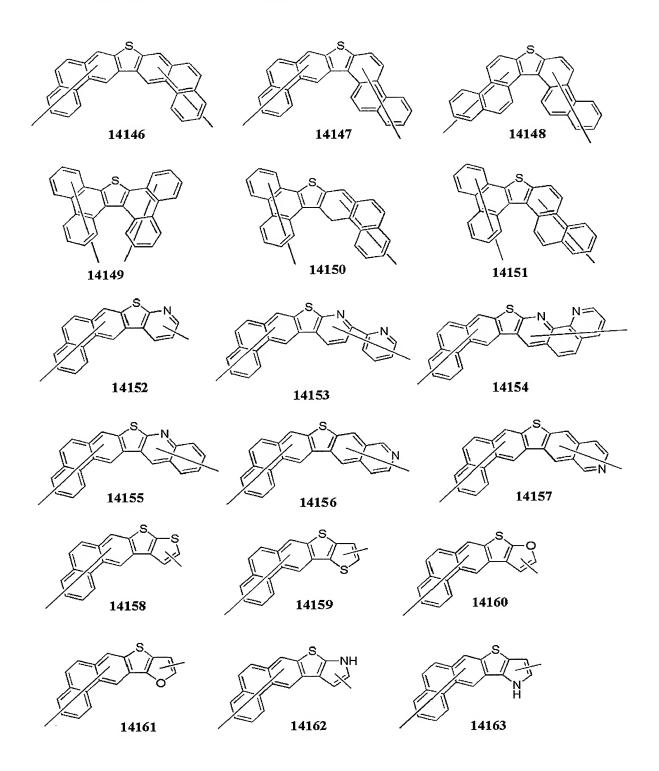
[0019]



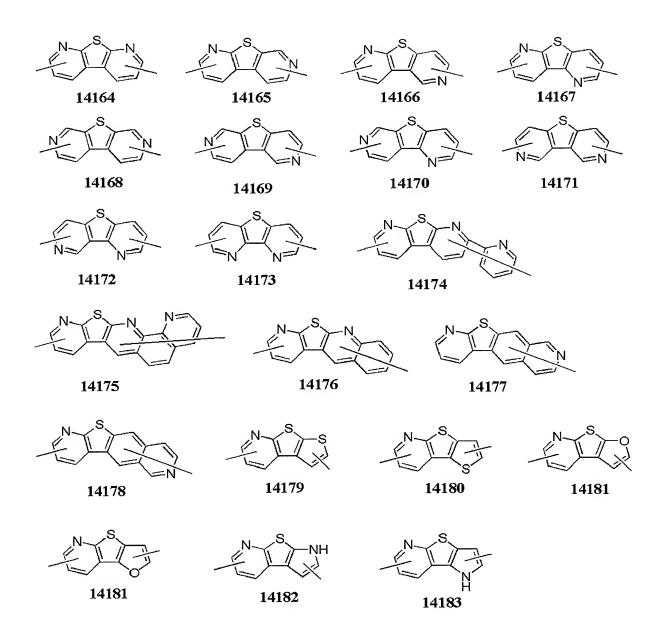
[0020]



[0021]

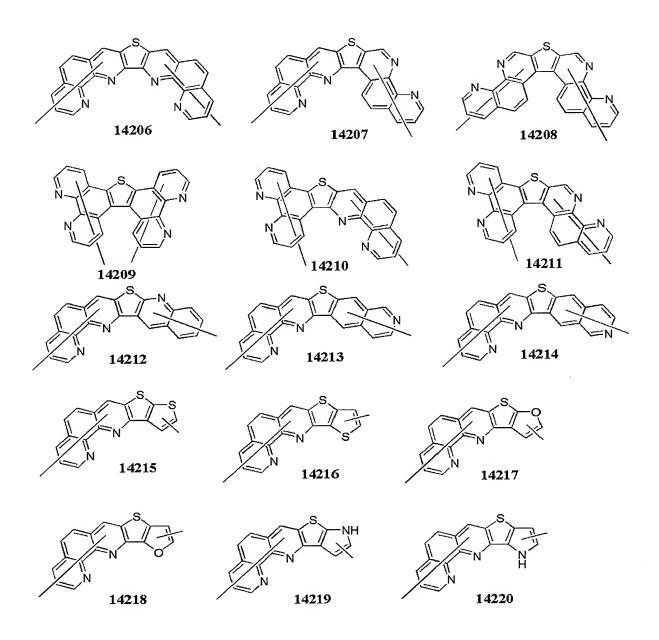


[0022]

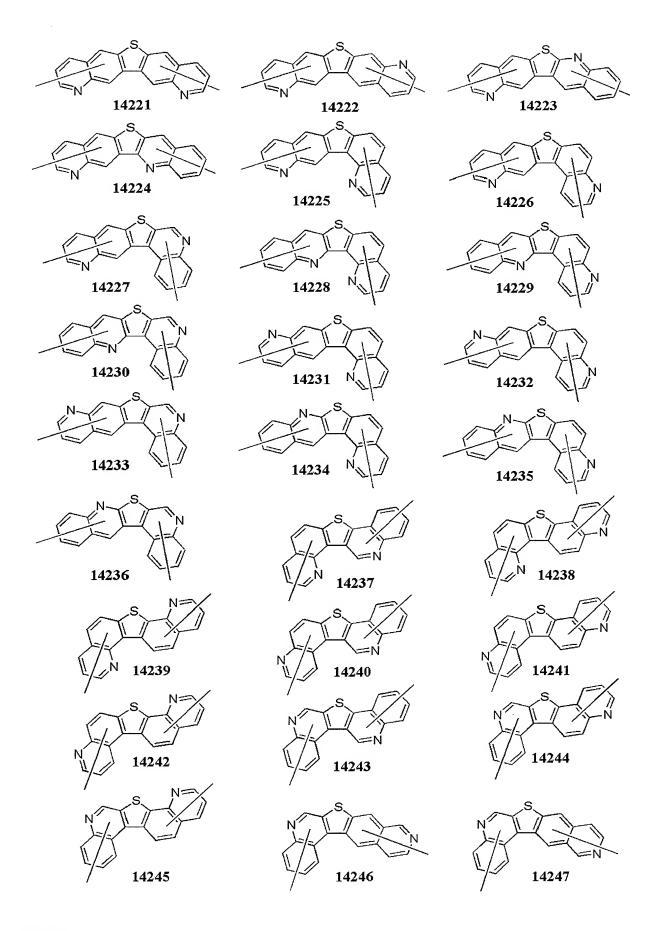


[0023]

[0024]



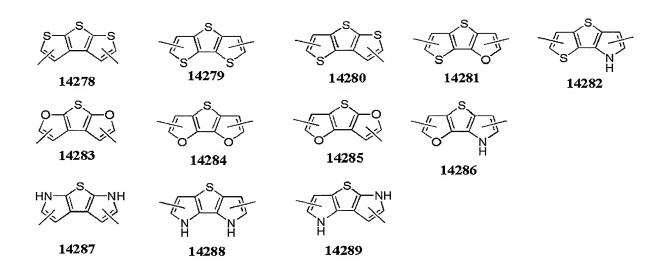
[0025]



[0026]

[0027]

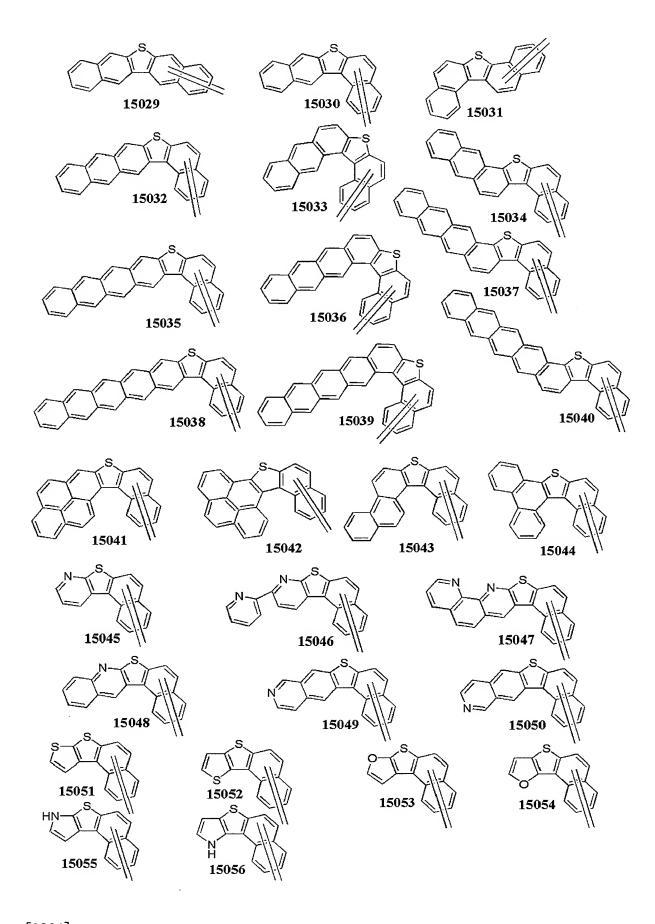
[0028]



[0029]

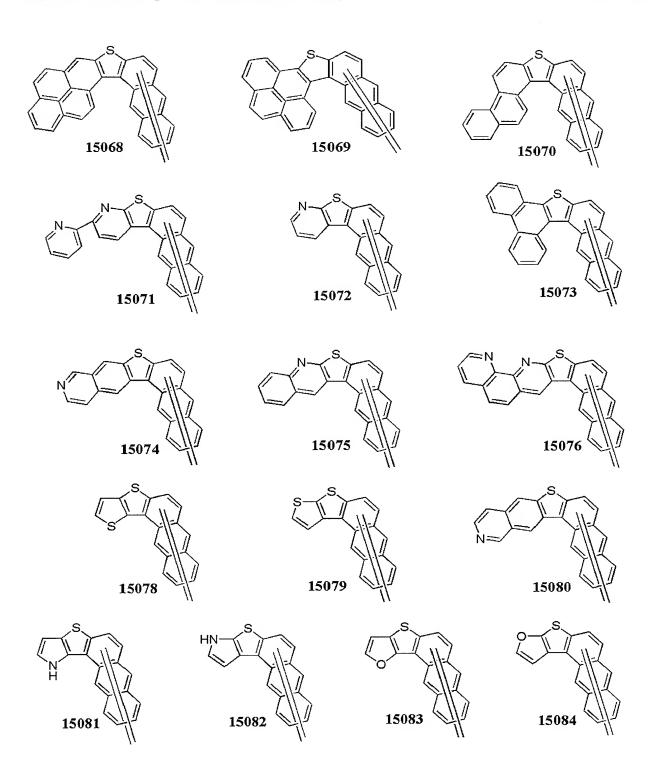
The following examples are given as an example of a formula (1-5).

[0030]

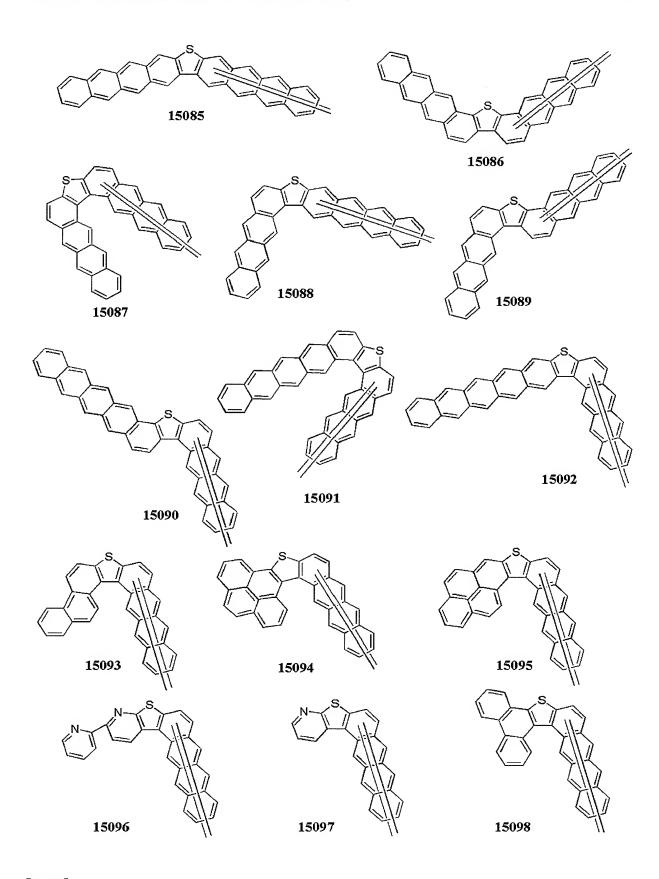


[0031]

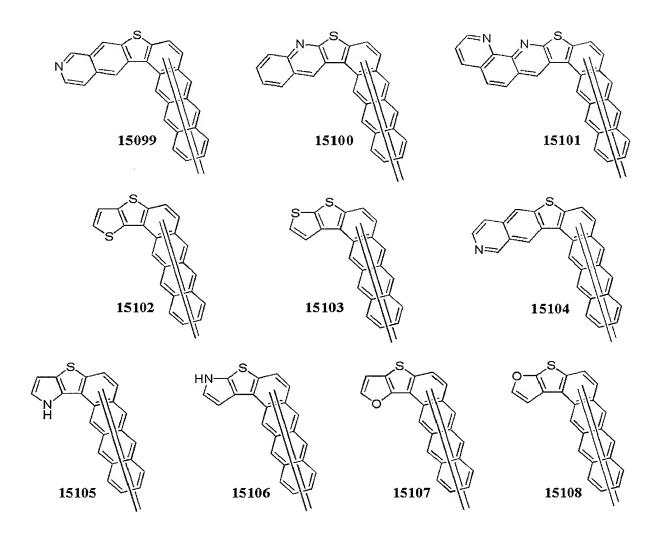
[0032]



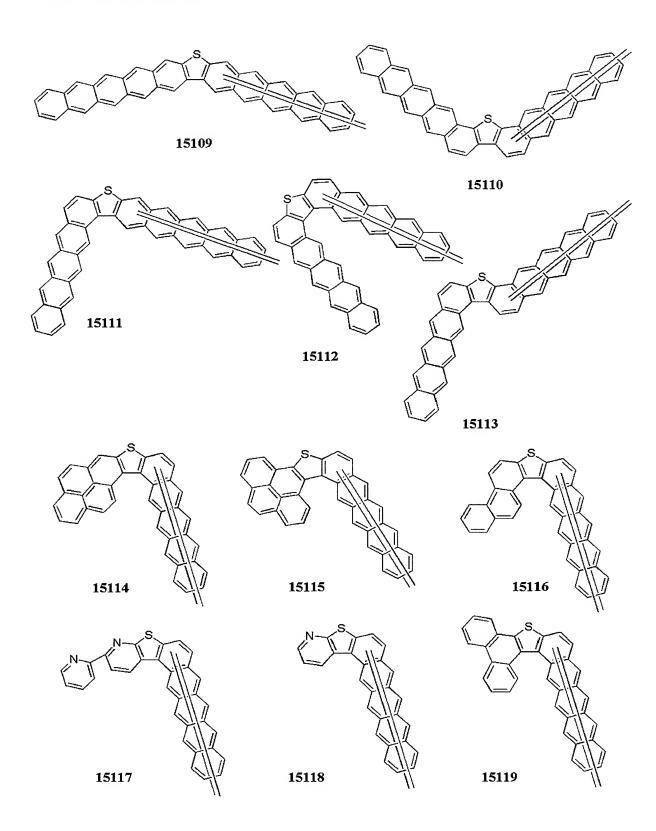
[0033]



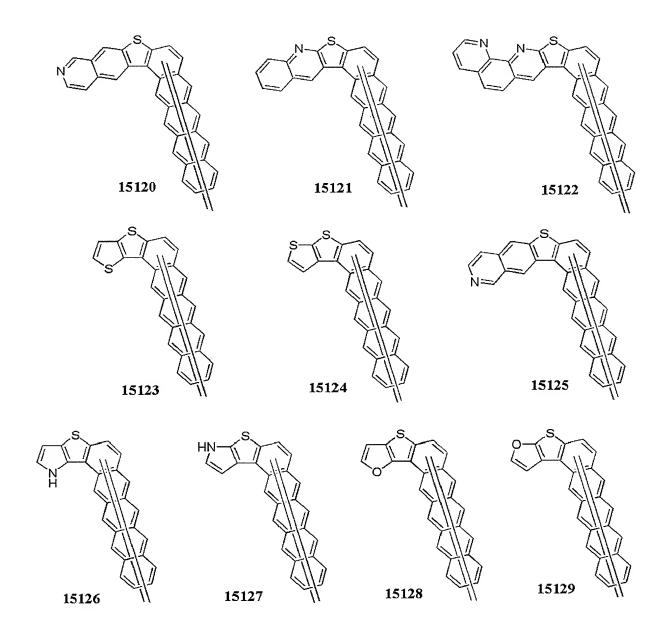
[0034]



[0035]

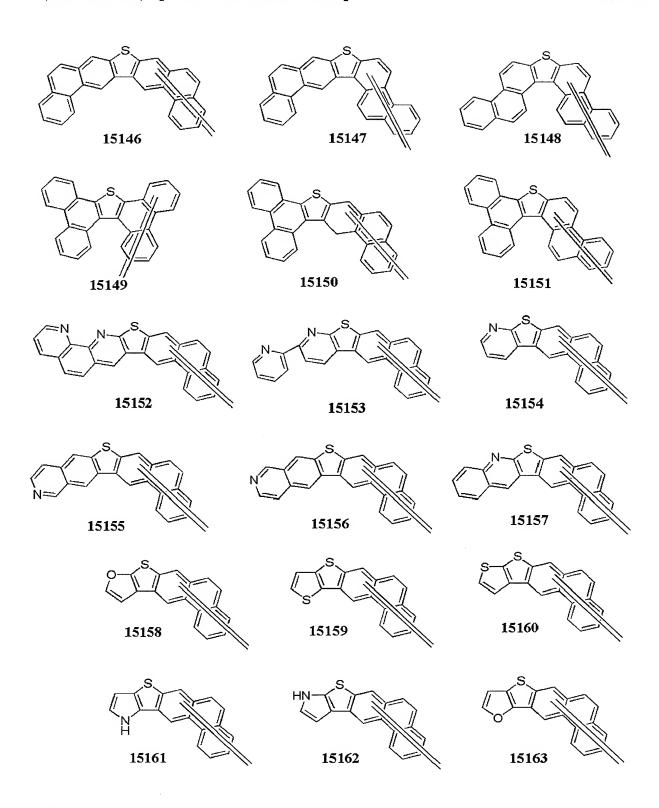


[0036]

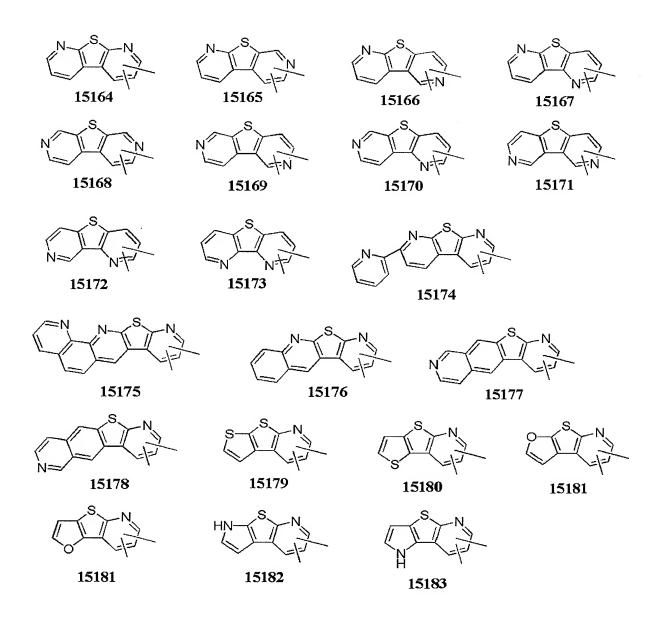


[0037]

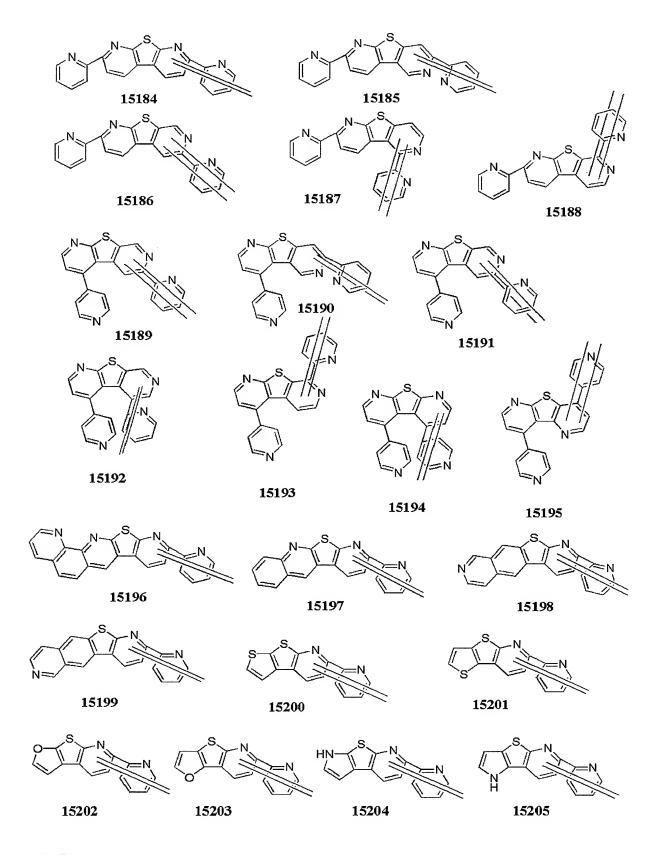
[0038]



[0039]



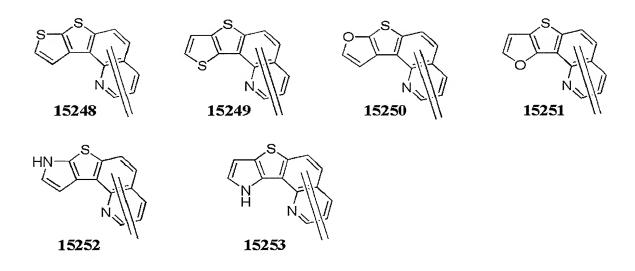
[0040]



[0041]

[0042]

[0043]



[0044]

[0045]

[0046]

[0047]

A repeating unit including the structure shown by the above-mentioned formula (1), (1-1), (1-2), (1-3), (1-4), or (1-5), On an aromatic ring and/or a thiophene ring, an alkyl group, an alkoxy group, An alkylthio group, an aryl group, an aryloxy group, an arylthio group, An arylated alkyl group, an aryl alkoxy group, an aryl alkylthio group, An aryl alkenyl group, an aryl alkynyl group, an amino group, a substituted amino group, It may have a substituent chosen from the group which consists of a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, and a cyano group. It can have a **** group on A ring, B ring, C ring, D ring, E ring, F ring, and G ring, and when it is the above-mentioned formula (1-1) and (1-2), it can have it also on a thiophene ring. When there are two or more substituents, they may be the same or may differ.

[0048]

As an alkyl group, a straight chain, branching, or annular any may be sufficient here. A carbon number is usually one to about 20, and are the carbon numbers 3-20 preferably. Specifically A methyl group, an ethyl group, a propyl group, i-propyl group, a butyl group, i-butyl group, t-butyl group, a pentyl group, a hexyl group, a cyclohexyl group, A heptyl group, an octyl group, a 2ethylhexyl group, a nonyl group, a decyl group, A 3,7-dimethyloctyl group, a lauryl group, a trifluoromethyl group, A pentafluoroethyl group, a perfluoro butyl group, a perfluoro hexyl group, a perfluoro octyl group, etc. are mentioned, and a pentyl group, a hexyl group, an octyl group, a 2ethylhexyl group, a decyl group, and a 3,7-dimethyloctyl group are preferred. [0049]

A straight chain, branching, or annular any may be sufficient as an alkoxy group. A carbon number is usually one to about 20, and are the carbon numbers 3-20 preferably. Specifically A methoxy group, an ethoxy basis, a propyloxy group, i-propyloxy group, A butoxy group, i-butoxy group, t-butoxy group, a pentyloxy group, A hexyloxy group, a cyclohexyloxy group, a heptyloxy group, an octyloxy group, 2-ethylhexyloxy group, a nonyloxy group, a decyloxy group, a 3,7dimethyl octyloxy group, A lauryl oxy group, a trifluoro methoxy group, a pentafluoro ethoxy basis, A perfluoro butoxy group, a perfluoro hexyl group, a perfluoro octyl group, A methoxymethyloxy group, a 2-methoxy ethyloxy group, etc. are mentioned, and a pentyloxy group, a hexyloxy group, an octyloxy group, 2-ethylhexyloxy group, a decyloxy group, and a 3,7dimethyl octyloxy group are preferred.

[0050]

A straight chain, branching, or annular any may be sufficient as an alkylthio group. A carbon number is usually one to about 20, and are the carbon numbers 3-20 preferably. Specifically A methylthio group, an ethyl thio group, a propyl thio group, and i-propyl thio group, A butyl thio

group, i-butyl thio group, t-butyl thio group, a pentyl thio group, A hexyl thio group, a cyclohexyl thio group, a heptyl thio group, an octylthio group, A 2-ethylhexyl thio group, a nonyl thio group, a decyl thio group, a 3,7-dimethyloctylthio group, A laurylthio group, a trifluoro methylthio group, etc. are mentioned and a pentyl thio group, a hexyl thio group, an octylthio group, a 2-ethylhexyl thio group, a decyl thio group, and a 3,7-dimethyloctylthio group are preferred. [0051]

A carbon number is usually six to about 60, and aryl groups are 7–48 preferably. Specifically, they are a phenyl group, C_1 – C_{12} alkoxyphenyl group (it is shown that C_1 – C_{12} are the carbon numbers 1–12.). The following is also the same. C_1 – C_{12} alkylphenyl group, 1–naphthyl group, 2–naphthyl group, 1–anthracenyl group, 2–anthracenyl group, 9–anthracenyl group, a pentafluorophenyl group, etc. are illustrated, and C_1 – C_{12} alkoxyphenyl group, C_1 – C_{12} alkylphenyl group are preferred. He is the atom group excluding [the aryl group] one hydrogen atom from aromatic hydrocarbon here. What a thing with a condensed ring, the independent benzene ring, or two or more condensed rings combined here via bases, such as direct or vinylene, as aromatic hydrocarbon is contained.

Carry out C_1 – C_{12} alkoxy ** and specifically, Methoxy and ethoxy ** propyloxy, i–propyloxy, butoxy, i–butoxy, pentyloxy one, hexyloxy one, cyclohexyloxy, heptyloxy, octyloxy, 2–ethylhexyloxy, nonyloxy, decyloxy one, 3,7–dimethyl octyloxy, lauryl oxy, etc. are illustrated. As C_1 – a C_{12} alkylphenyl group, specifically A methylphenyl group, An ethyl phenyl group, a dimethylphenyl group, a propyl phenyl group, a mesityl group, A methylethyl phenyl group, i–propyl phenyl group, a buthylphenyl group, i–buthylphenyl group, t–buthylphenyl group, a pentyl phenyl group, an isoamyl phenyl group, a hexyl phenyl group, a heptyl phenyl group, an octyl phenyl group, a nonylphenyl group, a decyl phenyl group, a dodecyl phenyl group, etc. are illustrated.

[0052]

As an aryloxy group, a carbon number is usually six to about 60, and are 7–48 preferably. Specifically A phenoxy group, C_1 – a C_{12} alkoxy phenoxy group, C_1 – C_{12} alkyl phenoxy group, a 1–naphthyloxy group, A 2–naphthyloxy group, a pentafluoro phenyloxy group, etc. are illustrated, and C_1 – a C_{12} alkoxy phenoxy group, C_1 – C_{12} alkyl phenoxy group are preferred. Carry out C_1 – C_{12} alkoxy ** and specifically, Methoxy and ethoxy ** propyloxy, i–propyloxy, butoxy, i–butoxy, pentyloxy one, hexyloxy one, cyclohexyloxy, heptyloxy, octyloxy, 2–ethylhexyloxy, nonyloxy, decyloxy one, 3,7–dimethyl octyloxy, lauryl oxy, etc. are illustrated. As C_1 – a C_{12} alkyl phenoxy group, specifically A methylphenoxy group, An ethyl phenoxy group, a dimethyl phenoxy group, i–propyl phenoxy group, a butylphenoxy group, i–butylphenoxy group, a pentyl phenoxy group, an isoamyl phenoxy group, a hexyl phenoxy group, a heptyl phenoxy group, an octyl phenoxy group, a nonyl phenoxy group, a decyl phenoxy group, a dodecyl phenoxy group, etc. are illustrated. [0053]

As an arylthio group, a carbon number is usually six to about 60, and are the carbon numbers 7–48 preferably. Specifically A phenylthio group, C_1 – a C_{12} alkoxy phenylthio group, C_1 – C_{12} alkyl phenylthio group, 1–naphthyl thio group, 2–naphthyl thio group, a pentafluoro phenylthio group, etc. are illustrated, and C_1 – a C_{12} alkoxy phenylthio group, C_1 – a C_{12} alkyl phenylthio group are preferred.

[0054]

A carbon number is usually seven to about 60, and arylated alkyl groups are 7–48 preferably. Specifically Phenyl–C $_1$ – C $_{12}$ alkyl group, C $_1$ – C $_{12}$ alkoxyphenyl C $_1$ – C $_{12}$ alkyl group, C $_1$ – C $_{12}$ alkyl group, 1–naphthyl C $_1$ – C $_{12}$ alkyl group, and 2–naphthyl C $_1$ – C $_{12}$ alkyl group, etc. are illustrated, C $_1$ – C $_{12}$ alkoxyphenyl C $_1$ – C $_{12}$ alkyl group, C $_1$ – C $_{12}$ alkylphenyl C $_1$ –

C₁₂ alkyl group are preferred.

[0055]

A carbon number is usually seven to about 60, and aryl alkoxy groups are the carbon numbers 7–48 preferably. Specifically A phenyl methoxy group, a phenylethoxy group, a phenylbutoxy group, A phenylpentyloxy group, a phenylhexyloxy group, a phenylheptyloxy group, Phenyl- C_1 , such as a phenyloctyloxy group, - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, and 2-naphthyl C_1 - C_{12} alkoxy group, etc. are illustrated, C_1 - C_{12} alkoxyphenyl C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, and C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group, C_1 - C_{12} alkoxy group are preferred.

[0056]

A carbon number is usually seven to about 60, and aryl alkylthio groups are the carbon numbers 7–48 preferably. Specifically Phenyl– C_1 – C_{12} alkylthio group, C_1 – C_{12} alkoxyphenyl C_1 – C_{12} alkylthio group, 1–naphthyl C_1 – C_{12} alkylthio group, and 2–naphthyl C_1 – C_{12} alkylthio group, etc. are illustrated, C_1 – C_{12} alkoxyphenyl C_1 – C_{12} alkylthio group, C_1 – C_{12} alkylthio group are preferred.

A carbon number is usually seven to about 60, and aryl alkenyl groups are the carbon numbers 7–48 preferably. Specifically Phenyl– C_2 – C_{12} alkenyl group, C_1 – C_{12} alkoxyphenyl C_2 – C_{12} alkenyl group, 1–naphthyl C_2 – C_{12} alkenyl group, and 2–naphthyl C_2 – C_{12} alkenyl group, etc. are illustrated, C_1 – C_{12} alkoxyphenyl C_2 – C_{12} alkenyl group, C_2 – C_{12} alkylphenyl C_1 – C_{12} alkenyl group are preferred. [0058]

A carbon number is usually seven to about 60, and aryl alkynyl groups are the carbon numbers 7–48 preferably. Specifically Phenyl– C_2 – C_{12} alkynyl group, C_1 – C_{12} alkoxyphenyl C_2 – C_{12} alkynyl group, 1–naphthyl C_2 – C_{12} alkynyl group, and 2–naphthyl C_2 – C_{12} alkynyl group, etc. are illustrated, C_1 – C_{12} alkoxyphenyl C_2 – C_{12} alkynyl group, etc. are illustrated, C_1 – C_{12} alkoxyphenyl C_2 – C_{12}

alkynyl group, C₁ - C₁₂ alkylphenyl C₂ - C₁₂ alkynyl group are preferred.

[0059]

A substituted amino group may say the amino group replaced by 1 or two bases which are chosen from an alkyl group, an aryl group, an arylated alkyl group, or a univalent heterocycle group, and this alkyl group, the aryl group, the arylated alkyl group, or the univalent heterocycle group may have a substituent. A carbon number is usually one to about 60 without including the carbon number of this substituent, and they are the carbon numbers 2-48 preferably. Specifically A methylamino group, a dimethylamino group, an ethylamino group, A diethylamino group, a propylamino group, a dipropylamino group, i-propylamino group, A diisopropylamino group, a butylamino group, i-butylamino group, t-butylamino group, A pentylamino group, a hexylamino group, a cyclohexylamino group, a heptylamino group, An octylamino group, a 2ethylhexyl amino group, a nonylamino group, A decylamino group, a 3,7-dimethyloctylamino group, a lauryl amino group, A cyclopentylamino group, a JISHIKURO pentylamino group, a cyclohexylamino group, A dicyclohexylamino group, a pyrrolidyl group, a piperidyl group, a ditrifluoromethyl amino group phenylamino group, A diphenylamino group, C_1 - a C_{12} alkoxy phenylamino group, A JI ($C_1 - C_{12}$ alkoxyphenyl) amino group, A JI ($C_1 - C_{12}$ alkylphenyl) amino group, 1-naphthyl amino group, 2-naphthyl amino group, a pentafluoro phenylamino group, a pyridylamino group, a pyridazinylamino group, a pyrimidyl amino group, a pyrazyl amino group, Triazyl amino group phenyl- C_1 - C_{12} alkylamino group, C_1 - C_{12} alkoxyphenyl C_1 - C_{12} alkylamino group, $C_1 - C_{12}$ alkylphenyl $C_1 - C_{12}$ alkylamino group, A JI $(C_1 - C_{12}$ alkoxyphenyl

 C_1 – C_{12} alkyl) amino group, JI (C_1 – C_{12} alkylphenyl C_1 – C_{12} alkylamino group and 1–naphthyl C_1 – C_{12} alkylamino group, and 2–naphthyl C_1 – C_{12} alkylamino group, etc. are illustrated. [0060]

A substitution silyl group says the silyl group replaced by 1, 2, or three bases which are chosen from an alkyl group, an aryl group, an arylated alkyl group, or a univalent heterocycle group, and a carbon number is usually one to about 60, and are the carbon numbers 3–48 preferably. This alkyl group, the aryl group, the arylated alkyl group, or the univalent heterocycle group may have a substituent.

Specifically A trimethylsilyl group, a triethyl silyl group, a TORIPURO pill silyl group, A tri–i–propyl silyl group, a dimethyl–i–pro pilus silyl group, a diethyl–i–propyl silyl group, t–butylsilyl dimethylsilyl group, a pentyl dimethylsilyl group, a hexyl dimethylsilyl group, A heptyl dimethylsilyl group, an octyl dimethylsilyl group, a 2–ethylhexyl dimethylsilyl group, A nonyl dimethylsilyl group, a decyl dimethylsilyl group, a 3,7–dimethyloctyl–dimethylsilyl group, Lauryl dimethylsilyl group and phenyl–C $_1$ – C $_{12}$ alkyl silyl group, C $_1$ – C $_{12}$ alkoxyphenyl C $_1$ – C $_{12}$ alkyl silyl group, C $_1$ – C $_{12}$ alkyl silyl group, and 2–naphthyl C $_1$ – C $_{12}$ alkyl silyl group, Phenyl–C $_1$ – C $_{12}$ alkyl dimethylsilyl group, a triphenyl silyl group, a trib–xylyl silyl group, a tribenzylsilyl group, a diphenylmethyl silyl group, t–butylphenylsilyl group, a dimethylphenyl silyl group, etc. are illustrated.

[0061]

As a halogen atom, a fluorine atom, a chlorine atom, a bromine atom, and iodine atoms are illustrated.

[0062]

A carbon number is usually two to about 20, and acyl groups are the carbon numbers 2–18 preferably. Specifically, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a pivaloyl group, benzoyl, a trifluoroacetyl group, pentafluoro benzoyl, etc. are illustrated. [0063]

A carbon number is usually two to about 20, and acyloxy groups are the carbon numbers 2–18 preferably. Specifically, an acetoxy group, a propionyloxy group, a butyryloxy group, an isobutyryloxy group, a pivaloyloxy group, a benzoyloxy group, a trifluoro acetyloxy group, a pentafluoro benzoyloxy group, etc. are illustrated.

[0064]

An imino group is about two to 20 carbon number, and are the carbon numbers 2–18 preferably. Specifically, the basis etc. which are shown with the following structural formulae are illustrated.

[0065]

A carbon number is usually two to about 20, and amide groups are the carbon numbers 2–18 preferably. Specifically A formamide group, an acetamide group, a PUROPIO amide group, A BUCHIRO amide group, a benzamide group, a trifluoro acetamide group, a pentafluoro benzamide group, A diformamide group, a diacetoamide group, the Zypro Pio amide group, a JIBUCHIRO amide group, a dibenzamide group, a JITORI fluoro acetamide group, a dipentafluorobenzamide group, etc. are illustrated.
[0066]

An imido group is usually about two to 60 carbon number, and are the carbon numbers 2-48 preferably. The basis specifically shown below is illustrated.

[0067]

A univalent heterocycle group means the remaining atom groups excluding one hydrogen atom from the heterocyclic compound, and a carbon number is usually four to about 60, and are 4–20 preferably. The carbon number of a substituent is not contained in the carbon number of a heterocycle group. The heterocyclic compound refers to that to which the element which constitutes a ring among organic compounds with cyclic structure contains hetero atoms, such as not only a carbon atom but oxygen, sulfur, nitrogen, phosphorus, boron, etc., in endocyclic here. Specifically A thienyl group, $C_1 - C_{12}$ alkyl thienyl group, A pyrrolyl group, a furil group, a pyridyl group, $C_1 - C_{12}$ alkyl pyridyl group, A piperidyl group, a quinolyl group, an isoquinolyl group, etc. are illustrated, and a thienyl group, $C_1 - C_{12}$ alkyl thienyl group, a pyridyl group are preferred.

[8900]

A substitution carboxyl group is usually about two to 60 carbon number, and are the carbon numbers 2–48 preferably. The carboxyl group replaced by the alkyl group, the aryl group, the arylated alkyl group, or the univalent heterocycle group is said, A methoxycarbonyl group, an ethoxycarbonyl group, a carbopropoxy group, i–carbopropoxy group, a butoxycarbonyl group, i–butoxycarbonyl group, A t–butoxycarbonyl group, a pentyloxy carbonyl group, a carbohexyloxy group, A cyclocarbohexyloxy group, a heptyloxy carbonyl group, an octyloxy carbonyl group, 2–ethylcarbohexyloxy group, a nonyloxy carbonyl group, A carbodecyloxy group, a 3,7–dimethyl octyloxy carbonyl group, A dodecyloxy carbonyl group, a trifluoromethoxycarbonyl group, A

[0069]

pentafluoro ethoxycarbonyl group, a perfluoro butoxycarbonyl group, a perfluoro hexyloxy carbonyl group, a perfluoro octyloxy carbonyl group, a phenoxy carbonyl group, a naphthoxy carbonyl group, a pyridyloxy carbonyl group, etc. are mentioned. This alkyl group, the aryl group, the arylated alkyl group, or the univalent heterocycle group may have a substituent. The carbon number of this substituent is not contained in the carbon number of a substitution carboxyl group.

In the basis which contains an alkyl chain among the above, They may be a straight chain, branching, annular either, or those combination, When it is not a straight chain, an isoamyl group, a 2-ethylhexyl group, a 3,7-dimethyloctyl group, a cyclohexyl group, $4-C_1-C_{12}$ alkyl cyclohexyl group, etc. are illustrated, for example. The tip of two alkyl chains is connected and the ring may be formed. Some of methyl groups and methylene groups of the alkyl chain may be replaced by the methyl group and methylene group which were replaced with the basis and one or more fluoride containing a hetero atom, and an oxygen atom, a sulfur atom, a nitrogen atom, etc. are illustrated as those hetero atoms.

When an aryl group and a heterocycle group are included among the examples of a substituent in the part, they may have one more or more substituents.
[0070]

As the example of what includes the structure shown by a formula (1-1) in a thiophene condensed ring unit,

[0072]

As the example of what includes the structure shown by a formula (1-2) in a thiophene condensed ring unit,

[0073]

$$C_8H_{17}O$$
 $C_8H_{17}O$
 $C_8H_{17}O$

[0074]

As the example of what includes the structure shown by a formula (1-3) in a thiophene condensed ring unit,

[0075]

As the example of what includes the structure shown by a formula (1-4) in a thiophene

condensed ring unit,

[0076]

$$(C_5H_{11})_2N$$
 $N(C_5H_{11})_2$

[0077]

[0078]

$$C_8H_{17}O$$
 OC_8H_{17} OC_8H_{17} OC_8H_{17} OC_8H_{17}

[0079]

[0800]

[0081]

As the example of what includes the structure shown by a formula (1-5) in a thiophene condensed ring unit,

[0082]

[0083]

Among a formula, as for Me, a methyl group and Ph express a phenyl group, Bn expresses benzyl, and Ac expresses an acetyl group, respectively.

[0086]

In the above-mentioned formula (1), (1-1), (1-2), (1-3), (1-4), or (1-5), An aromatic ring and/or a thiophene ring An alkyl group, an alkoxy group, an alkylthio group, An aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, An aryl alkoxy group, an aryl alkylthio group, an aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, A halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, It is preferred to have a substitution carboxyl group, and cyano group from the viewpoint which improves the solubility of a high molecular compound, the viewpoint to which a luminous wavelength is changed, a viewpoint of raising luminous efficiency,

etc.

As this substituent, an alkyl group, an alkoxy group, an alkylthio group, An aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, An aryl alkoxy group, an aryl alkylthio group, a substituted amino group, a substitution silyl group, A fluorine atom, an acyl group, an acyloxy group, an amide group, an imido group, a univalent heterocycle group, A carboxyl group, a substitution carboxyl group, and a cyano group are preferred, and an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an arylated alkyl group, an aryl alkoxy group, and an aryl alkylthio group are still more preferred especially.

In [in / specifically / the above-mentioned formula (1-1)] (1-2) on A ring and/or a thiophene ring, On B ring and/or a thiophene ring, it is preferred to have in (1-5) in (1-4) on C ring at F ring and/or G ring top in (1-3) on D ring and/or E ring. [0087]

the high molecular compound of this invention — a thiophene condensed ring unit — one sort — or two or more sorts are included.

In a thiophene condensed ring unit, although thiophene condensed ring structure may be in the portion used as the main chain of a high molecular compound including this unit and it may be in the portion used as a side chain, it is preferred that it is in the portion used as a main chain. [0088]

The following structures are illustrated as an example in case thiophene condensed ring structure is in a main chain.

[0089]

The following structures are illustrated as an example in the case of being in a side chain.

In a thiophene condensed ring unit, the repeated structure unit which consists only of thiophene condensation structure is preferred.

In the high molecular compound of this invention, it is preferred that a thiophene condensed ring unit is a repeating unit including the structure shown by the formula (1-1) or a formula (1-4). What has only aromatic hydrocarbon rings is preferred as a P loop, Q ring, A ring, B ring, C ring, D ring, E ring, F ring, and a G ring.

Especially, that in which a thiophene condensed ring unit has only aromatic hydrocarbon rings as A ring, B ring, C ring, D ring, E ring, F ring, and a G ring including the structure shown by the above, a formula (1-1), or a formula (1-4) is preferred. In a formula (1-1), it is more preferably,

$$(R_3)_c$$
 $(R_4)_d$

Come out and it is, In the inside of a formula <1-4>

$$(R_1)_a$$
 $(R_2)_b$

$$(R_5)_e$$
 $(R_6)_f$

$$(2-3)$$

$$(2-4)$$

$$(R_9)_i$$
 $(R_{10})_j$

(2-6)

It comes out. [0090]

The inside of a formula, R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂, Independently, respectively An alkyl group, an alkoxy group, an alkylthio group, an arylated alkyl group, an arylalkoxy group, An arylalkylthio group, an arylalkenyl group, an arylalkynyl group, An amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, or a substitution carboxyl group is shown. a and b show the integer of 0–3 independently, respectively. c shows 0 or 1. d shows the integer of 0–3. e, f, g, and h show the integer of 0–5 independently, respectively. [0091]

From the viewpoint which improves solubility, the viewpoint to which a luminous wavelength is changed, a viewpoint which raises luminous efficiency, etc. As for that a repeating unit has a substituent, i.e., a+b of a formula (2-1), c+d of a formula (2-2), e+f of a formula (2-3), g+h of a formula (2-4), i+j of a formula (2-5), and k+l of a formula (2-6), it is preferred that it is one or more.

[0092]

When there are two or more $R_{1 \text{ and}} R_2$, R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_{9} , R_{10} , R_{11} , and R_{12} , respectively, they may be the same or may differ. [0093]

In the repeating unit chosen from the above (2-1), (2-2), (2-3), (2-4), (2-5), and (2-6), In [the repeating unit shown by a formula (2-1) is preferred, and] a formula (2-1), R_1 and/or R_2 A with a carbon numbers of three or more alkyl group, The case of a with a carbon numbers of three or more alkylthio group, an aryl group, an aryloxy group, an arylated alkyl group, an aryl alkoxy group, an arylakylthio group, and a univalent heterocycle group is more preferred. [0094]

The sum total of all the repeating units which the high molecular compound of this invention has is usually less than more than 1 mol %100 mol %, as for the quantity of a thiophene condensed ring unit, it is preferred that it is more than 20 mol %, and it is still more preferred that it is less than more than 30 mol %90 mol %.

[0095]

The high molecular compound of this invention has a preferred copolymer including the copolymer of the things which have a different substituent from a viewpoint which raises fluorescence intensity, and which have the same thiophene condensed ring structure or a thiophene condensed ring unit, and at least one or more kinds of other repeating units. As a repeating unit, the repeating unit shown by the following formula (3), the formula (4), the formula (5), or a formula (6) is preferred except a thiophene condensed ring unit. (5)

$$-(A r 2 - X 1)_{f} - A r 3 - (4)$$

$$-Ar_4-X_2-(5)$$

 $-X_3-(6)$

Ar₁, Ar₂, Ar₃, and Ar₄ show among a formula the divalent basis which has an allylene group, a divalent heterocycle group, or metal complex structure independently, respectively. X $_1$, X $_2$, and X $_3$ show $-CR_{13}=CR_{14}-$, -C**C-, $-N(R_{15})-$, or $-(SiR_{16}R_{17})_m$ independently, respectively. R_{13} and R_{14} show a hydrogen atom, an alkyl group, an aryl group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group independently, respectively. R_{15} , R_{16} , and R_{17} show a hydrogen atom, an alkyl group, an aryl group, a univalent heterocycle group, an arylated alkyl group, or a substituted amino group independently, respectively. If shows the integer of 0–2. m shows the integer of 1–12. When two or more R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} exist, respectively, they may be the same or may differ. [0096]

It is the atom group excluding two hydrogen atoms from aromatic hydrocarbon, a carbon number is usually six to about 60, and allylene groups are 6-20 preferably. What a thing with a condensed ring, the independent benzene ring, or two or more condensed rings combined here via bases, such as direct or vinylene, as aromatic hydrocarbon is contained.

[0099]

[0101]

[0102]

[0103]

A divalent heterocycle group means the remaining atom groups excluding two hydrogen atoms from the heterocyclic compound, and a carbon number is usually three to about 60.

The heterocyclic compound refers to that to which the element which constitutes a ring among organic compounds with cyclic structure contains hetero atoms, such as not only a carbon atom but oxygen, sulfur, nitrogen, Lynn, boron, arsenic, etc., in endocyclic here.
[0104]

As a divalent heterocycle group, the following are mentioned, for example.

The divalent heterocycle group which contains nitrogen as a hetero atom; A pyridinediyl group (formulas 39–44 of the following figure), A diaza phenylene group (formulas 45–48 of the following figure), a quinolinediyl group (formulas 49–63 of the following figure), A quinoxalinediyl group (formulas 64–68 of the following figure), an acridinediyl group (formulas 69–72 of the following figure), a bipyridyldiyl group (formulas 73–75 of the following figure), a phenanthrolinediyl group (formulas 76–78 of the following figure), etc.

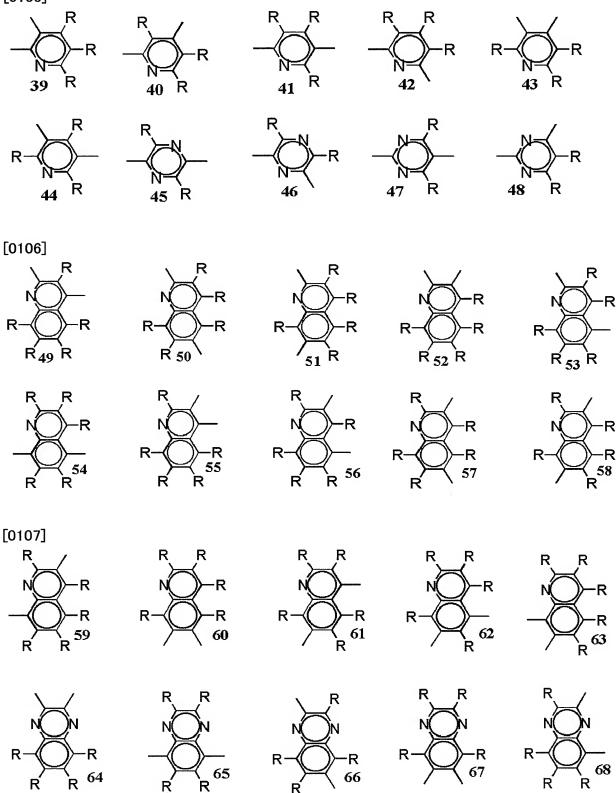
The basis which has fluorene structure including a silicon, nitrogen, selenium, etc. as a hetero atom (formulas 79-93 of the following figure).

Five-membered ring heterocycle group: (formulas 94-98 of the following figure) which contains a silicon, nitrogen, sulfur, selenium, etc. as a hetero atom is mentioned.

Five-membered ring condensation complex group: (formulas 99-108 of the following figure) which contains a silicon, nitrogen, selenium, etc. as a hetero atom is mentioned.

Basis: (formulas 109-113 of the following figure) which joins together according to the alpha position of the hetero atom by the five-membered ring heterocycle group which contains a silicon, nitrogen, sulfur, selenium, etc. as a hetero atom, and has become a dimer and oligomer is mentioned.

Basis: (formulas 113–119 of the following figure) combined with the phenyl group according to the alpha position of the hetero atom by the five-membered ring heterocycle group which contains a silicon, nitrogen, sulfur, selenium, etc. as a hetero atom is mentioned. Basis: (formulas 120–125 of the following figure) which the phenyl group, the furil group, and the thienyl group replaced by the five-membered ring condensation heterocycle group which contains oxygen, nitrogen, sulfur, etc. as a hetero atom is mentioned. [0105]



[0111]

[0113]

[0114]

[0115]

In this invention, the divalent basis which has metal complex structure is the remaining divalent basis excluding two hydrogen atoms from the organic ligand of the metal complex which has an organic ligand.

The carbon number of this organic ligand is four to about 60, and usually For example, an eight

quinolinol and its derivative, Benzoquinolinol and its derivative, 2-phenyl-pyridine and its derivative, 2-phenyl-benzothiazole and its derivative, 2-phenyl-BENZOKI Southall and its derivative, porphyrin, its derivative, etc. are mentioned.

As a central metal of this complex, aluminum, zinc, beryllium, iridium, platinum, gold, europium, a terbium, etc. are mentioned, for example.

As a metal complex which has an organic ligand, a metal complex publicly known as a low-molecular fluorescent material and a phosphorescence material, a triplet emission complex, etc. are mentioned.

[0116]

Specifically as a divalent basis which has metal complex structure, following (126-132) are illustrated.

[0117]

In the example shown by the above-mentioned formulas 1-132, independently R, respectively A hydrogen atom, An alkyl group, an alkoxy group, an alkylthio group, an aryl group, an aryloxy

group, An arylthio group, an arylated alkyl group, an aryl alkoxy group, an aryl alkylthio group, An aryl alkenyl group, an aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. The carbon atom which the basis of the formulas 1–132 has may be replaced with the nitrogen atom, the oxygen atom, or the sulfur atom, and the hydrogen atom may be replaced by the fluorine atom.

[0118]

In the repeating unit shown by the above-mentioned formula (3), the repeating unit shown by the following formula (7), the formula (8), the formula (9), the formula (10), the formula (11), or a formula (12) is preferred.

$$\begin{array}{c}
\begin{pmatrix}
R_{18}\\
\\
-
\end{pmatrix}_{n} \\
-
\end{array}$$
(7)

[R_{18} among a formula An alkyl group, an alkoxy group, an alkylthio group, An aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, An aryl alkoxy group, an aryl alkylthio group, an aryl alkenyl group, An aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. n shows the integer of 0–4. When two or more R_{18} exists, they may be the same or may differ.]

[R $_{19}$ and R $_{20}$ among a formula, Independently, respectively An alkyl group, an alkoxy group, an alkylthio group, an aryl group, An aryloxy group, an arylthio group, an arylated alkyl group, an aryl alkoxy group, An aryl alkylthio group, an aryl alkenyl group, an aryl alkynyl group, An amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. o and p show the integer of 0–3 independently, respectively. When two or more R $_{19}$ and R $_{20}$ exist, respectively, they may be the same or may differ.]

$$\begin{array}{c|c}
\begin{pmatrix}
R_{21} \\
q
\end{pmatrix}_{q} \\
R_{22}
\\
R_{23}
\\
\begin{pmatrix}
R_{24} \\
r
\end{pmatrix}_{r}$$
(9)

[R₂₁ and R₂₄ among a formula, Independently, respectively An alkyl group, an alkoxy group, an alkylthio group, an aryl group, An aryloxy group, an arylthio group, an arylated alkyl group, an aryl alkoxy group, An aryl alkylthio group, an aryl alkenyl group, an aryl alkynyl group, An amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. q and r show the integer of 0–4 independently, respectively. R₂₂ and R₂₃ show a hydrogen atom, an alkyl group, an aryl group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group independently, respectively. When two or more R₂₁ and R₂₄ exist, they may be the same or may differ.]

[R₂₅ among a formula An alkyl group, an alkoxy group, an alkylthio group, An aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, An aryl alkoxy group, an aryl alkylthio group, an aryl alkenyl group, An aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. s shows the integer of 0–2. Ar₁₃ and Ar₁₄ show the divalent basis which has an allylene group, a divalent heterocycle group, or metal complex structure independently, respectively. ss and tt show 0 or 1 independently, respectively.

X $_4$ shows O, S, SO, SO $_2$, Se, or Te. When two or more R $_{25}$ exists, they may be the same or may differ.]

$$\begin{pmatrix} R_{26} \\ t \end{pmatrix}_{t} \qquad \chi_{6} \qquad \chi_{7} \qquad \begin{pmatrix} R_{27} \\ t \end{pmatrix}_{u}$$

$$\chi_{5} \qquad \chi_{7} \qquad \chi$$

 $[R_{26} \text{ and } R_{27} \text{ among a formula, Independently, respectively An alkyl group, an alkoxy group, an alkylthio group, an aryl group, An aryloxy group, an arylthio group, an arylated alkyl group, an arylalkoxy group, An aryl alkylthio group, an arylalkenyl group, an arylalkynyl group, An amino group,$

a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. t and u show the integer of 0–4 independently, respectively. X $_5$ shows O, S, SO $_2$, Se, Te, N–R $_{28}$, or SiR $_{29}$ R $_{30}$. X $_6$ and X $_7$ show N or C–R $_{31}$ independently, respectively. R $_{28}$, R $_{29}$, R $_{30}$, and R $_{31}$ show a hydrogen atom, an alkyl group, an aryl group, an arylated alkyl group, or a univalent heterocycle group independently, respectively. When two or more R $_{26}$, R $_{27}$, and R $_{31}$ exist, they may be the same or may differ.]

As an example of the five-membered ring of the center of the repeating unit shown by a formula (11), thiadiazole, oxadiazole, triazole, a thiophene, a franc, silole, etc. are mentioned. [0119]

$$\begin{array}{c}
\left(\begin{array}{c}
R_{32}\right)_{V} \\
= \left(\begin{array}{c}
R_{33} \\
R_{34}
\end{array}\right)_{R_{36}}
\end{array}$$

$$\begin{array}{c}
R_{35} \\
R_{36} \\
R_{37} \\
W
\end{array}$$
(13)

[R $_{32}$ and R $_{37}$ among a formula, Independently, respectively An alkyl group, an alkoxy group, an alkylthio group, an aryl group, An aryloxy group, an arylthio group, an arylated alkyl group, an aryl alkoxy group, An aryl alkylthio group, an aryl alkenyl group, an aryl alkynyl group, An amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. v and w show the integer of 0–4 independently, respectively. R_{33} , R_{34} , R_{35} , and R_{36} show a hydrogen atom, an alkyl group, an aryl group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group independently, respectively. Ar_{5} shows the divalent basis which has an allylene group, a divalent heterocycle group, or metal complex structure. When two or more R_{32} and R_{37} exist, they may be the same or may differ.]

In the repeating unit shown by the above-mentioned formula (4), the repeating unit shown with a following formula (13) is preferred.

Formula (13)

[Ar $_6$, Ar $_7$, Ar $_8$, and Ar $_9$ show an allylene group or a divalent heterocycle group independently among a formula, respectively. Ar $_{10}$, Ar $_{11}$, and Ar $_{12}$ show an aryl group or a univalent heterocycle group independently, respectively. Ar $_6$, Ar $_7$, Ar $_8$, Ar $_9$, and Ar $_{10}$ may have a substituent. x and y

show 0 or 1 independently, respectively, and are $0 \le x+y \le 1$. [0120]

As an example of the repeating unit shown by the above-mentioned formula (13), what is shown by the following (formulas 133-140) is mentioned.

[0121]

[0122]

[0123]

In the above-mentioned formula, R is the same as it of said formulas 1-132. In the above-mentioned example, although it has two or more R in one structural formula, they may be the same and may be different bases. In order to improve the solubility to a solvent, it is preferred to have except [one or more] a hydrogen atom, and it is preferred that there is little symmetry of the shape of a repeating unit including a substituent.

When R contains an aryl group and a heterocycle group in the above-mentioned formula in the part, they may have one more or more substituents.

In the substituent in which R contains an alkyl chain in the above-mentioned formula, They may be a straight chain, branching, annular either, or those combination, When it is not a straight chain, an isoamyl group, a 2-ethylhexyl group, a 3,7-dimethyloctyl group, a cyclohexyl group, 4- $\rm C_1$ alkyl cyclohexyl group, etc. are illustrated, for example. In order to improve the solubility to the solvent of a high molecular compound, it is preferred that the alkyl chain which has annular or branching or more in one is contained.

Two or more R may connect and the ring may be formed. In the case of the basis in which R contains an alkyl chain, this alkyl chain may be interrupted for the basis containing a hetero atom. As a hetero atom, an oxygen atom, a sulfur atom, a nitrogen atom, etc. are illustrated here.

[0124]

The repeating unit especially shown with a following formula (13-2) is preferred.

$$\begin{array}{c}
\begin{pmatrix}
R_{50} \\
hh
\end{pmatrix}_{hh} \\
\begin{pmatrix}
R_{51} \\
\vdots
\end{pmatrix}_{ii} \\
\begin{pmatrix}
R_{52} \\
\vdots
\end{pmatrix}_{ii}$$
(13-2)

 $[R_{50}, R_{51}]$, and R_{52} among a formula, Independently, respectively An alkyl group, an alkoxy group, an alkylthio group, an aryl group, An aryloxy group, an arylthio group, an arylated alkyl group, an aryl alkoxy group, An aryl alkylthio group, an aryl alkenyl group, an aryl alkynyl group, An amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. hh, ii, and ji

show the integer of 0-4 independently, respectively. z shows the integer of 1-2. When there are two or more R_{50} , R_{51} , and R_{52} , they may be the same or may differ.]

[0125]

The high molecular compound of this invention is a range which spoils neither a luminescent characteristic nor the charge transport characteristic, and may include repeating units other than the repeating unit shown by the thiophene condensed ring unit and the formula (3) – a formula (13). These repeating unit and other repeating units may be connected in the unit of non-conjugate, and those disconjugation portions may be contained in the repeating unit. As geometry, the thing shown below, the thing which combined two or more of what is shown below, etc. are illustrated. Here, R is a basis chosen from the same substituent as the aforementioned thing, and Ar shows the hydrocarbon group of 6–60 carbon numbers.

[0126]

What consists of a repeating unit substantially shown by the above-mentioned formula (1-1), (1-2), (1-3), (1-4), and/or (1-5) in the high molecular compound of this invention, What consists or more [of the repeating unit substantially shown by the above-mentioned formula (1-1), (1-2), (1-3), (1-4) and/or (1-5), and above-mentioned formula (3) - (13)] of one is preferred. [0127]

The high molecular compound of this invention may be randomness, a block, or a graft copolymer, and may be the polymers which have those interim structures, for example, the random copolymer which is tinged with block nature. From a viewpoint of obtaining a polymers photogen with a high quantum yield of fluorescence or a phosphorescence, a random copolymer, and the block or graft copolymer which is tinged with block nature is more preferred than a perfect random copolymer. A main chain has branching and the case where there are three or more end pieces, and a dendrimer are also contained. [0128]

Since a luminescent characteristic and a life when an element is used may fall if the polymerization activity group remains as it is, the end group of the high molecular compound of this invention may be protected by the stable basis. What has the conjugated bond which followed the conjugate structure of the main chain is preferred, for example, the structure combined with the aryl group or the heterocycle group via carbon-carbon bonding is illustrated. Specifically, the substituent of a statement, etc. are illustrated by ** 10 of JP,9-45478,A. [0129]

The number average molecular weights of polystyrene conversion of the high molecular

compound of this invention are 10 3 – 10 8 , and are 10 4 – 10 6 preferably. The weight average molecular weight of polystyrene conversion is 10 3 – 10 8 , and is 5x10 4 – 5x10 6 preferably. [0130]

As a good solvent to the high molecular compound of this invention, chloroform, a methylene chloride, a dichloroethane, a tetrahydrofuran, toluene, xylene, mesitylene, a tetralin, a decalin, n-butylbenzene, etc. are illustrated. Although based also on the structure and the molecular weight of a high molecular compound, it can be made to usually dissolve in these solvents 0.1% of the weight or more.

[0131]

Next, the manufacturing method of the high molecular compound of this invention is explained. . The high molecular compound of this invention corresponds per thiophene (method A) condensed ring. The method of carrying out the condensation polymerization of the compound which has a substituent in which two condensation polymerizations are possible; (method B) It corresponds to thiophene sulfone units (unit from which the thiophene structure of the thiophene condensed ring unit turned into thiophene sulfone structure), The substituent in which two condensation polymerizations are possible. The compound which it has. The polymer produced by making carry out a condensation polymerization. How to return; (method C) by the method of returning the polymer produced by making carry out the condensation polymerization of the compound which has a substituent corresponding to a thiophene sulfoxide unit (unit from which the thiophene structure of the thiophene condensed ring unit turned into thiophene sulfoxide structure) in which two condensation polymerizations are possible, etc. It can manufacture.

[0132]

For example, the high molecular compound of this invention,

Formula (14)

$$Y_1 - U - Y_2$$

[U shows among a formula the repeating unit shown by the above-mentioned formula (1), (1-1), (1-2), (1-3), (1-4), or (1-5). Y_1 and Y_2 express the substituent in which a condensation

polymerization is independently possible respectively.

It can manufacture by coming out and carrying out a condensation polymerization, using the compound shown as one of the raw materials (method A).
[0133]

The compound shown as a compound shown by the above-mentioned formula (14) by a following formula (15-1), (15-2), and (15-3)

$$Y_{11}$$
 Y_{12} Y_{13} Y_{14} Y_{15} Y_{16} Y_{15} Y_{16} Y_{16} Y_{17} Y_{18} Y_{19} Y

Formula (15-1) Formula (15-2) Formula (15-3)

 $[Y_{11}, Y_{12}, Y_{13}, Y_{14}, Y_{15}]$, and Y_{16} show among a formula the substituent in which a condensation polymerization is independently possible respectively. R_{38} , R_{39} , R_{40} , R_{41} , Independently R_{42} and

 R_{43} , respectively An alkyl group, An alkoxy group, an alkylthio group, an aryl group, an aryloxy group, an arylthio group, An arylated alkyl group, an aryl alkoxy group, an aryl alkylthio group, An aryl alkenyl group, an aryl alkynyl group, an amino group, a substituted amino group, a silyl group, a substitution silyl group, a halogen atom, an acyl group, an acyloxy group, an imino group, an amide group, an imido group, a univalent heterocycle group, a carboxyl group, a substitution carboxyl group, or a cyano group is shown. aa and bb show the integer of 0–3 independently, respectively. cc and dd show the integer of 0–5 independently, respectively. ee and gg show the integer of 0–7 independently, respectively. Each of aa+bb, cc+dd, and ee+gg is one or more. When two or more R_{38} , R_{39} , R_{40} , R_{41} , R_{42} , and R_{43} exist, respectively, they may be the same or may differ.]

[0134]

By coming out and using the compound shown, it is a following formula (15-4) and (15-5) (15-6), respectively,

The high molecular compound which comes out and has a repeating unit shown can be obtained. It is desirable following (15-7), (15-8), or (15-9) as a compound shown by a following formula (15-1), (15-2), or (15-3),

$$Y_{17}$$
 Y_{18} Y_{19} Y_{20} Y_{21} Y_{22} Y_{21} Y

 Y_{17} , Y_{18} , Y_{20} , Y_{21} , and Y_{22} among a formula, Independently, respectively A halogen atom, an alkyl sulfonate group, an aryl sulfonate group, An arylated alkyl sulfonate group, an ester-of-boric-acid group, a sulfonium methyl group, a phosphonium methyl group, a phosphonate methyl group, a mono- halogenation methyl group, a boric acid group, a formyl group, a cyano group, and a vinyl group are shown. R_{53} , R_{54} , R_{55} , R_{56} , R_{57} , and R_{58} , Independently, respectively A with a carbon numbers of three or more alkyl group, a with a carbon numbers of three or more alkyl group, an aryl group, an aryloxy group, an arylated alkyl group, an aryl alkoxy group, an aryl alkylthio group, a with a carbon numbers of four or more substituted amino group, and a with a carbon numbers of six or

more substitution silyl group are shown.

kk and II show the integer of 0–3 independently, respectively. mm and nn show the integer of 0–5 independently, respectively. oo and pp show the integer of 0–7 independently, respectively. Each of kk+II, mm+nn, and oo+pp is one or more. When two or more R_{53} , R_{54} , R_{55} , R_{56} , R_{57} , and R_{58} exist, they may be the same or may differ.

It is a compound shown with a following formula (15-10) still more preferably.

(15 - 10)

[Y_{23} and Y_{24} show a bromine atom, a chlorine atom, an alkyl sulfonate group, an aryl sulfonate group, an arylated alkyl sulfonate group, an ester-of-boric-acid group, a sulfonium methyl group, a phosphonium methyl group, a phosphonate methyl group, and a boric acid group among a formula. Independently R_{69} and R_{70} , respectively A with a carbon numbers of three or more alkyl group, A with a carbon numbers of three or more alkoxy group, a with a carbon numbers of three or more alkylthio group, an aryl group, an aryloxy group, an arylthio group, an arylated alkyl group, an aryl alkoxy group, an aryl alkylthio group, a with a carbon numbers of four or more substituted amino group, and a with a carbon numbers of six or more substitution silyl group are shown. qq and rr show the integer of 0–3 independently, respectively, and qq+rr is one or more. When two or more R_{69} and R_{70} exist, they may be the same or may differ.]

[0135]

High molecular compound of this invention, Compound shown with a following formula (20) Formula (20)

$$Y_1 - V - Y_2$$

[V shows among a formula the repeating unit which has the thiophene sulfone structure corresponding to the above-mentioned U. Y_1 and Y_2 are as aforementioned.]

After coming out and carrying out the condensation polymerization of the compound shown, it can manufacture also by returning (method B). Reduction can be performed according to the method of the reduction in the manufacturing method of the compound of (14) from the compound of the below-mentioned formula (20).

The repeating unit V which has the thiophene sulfone structure corresponding to each U is as follows.

[0136]

U

V

式(1-5)

式(20-5)

[0137]

For example, it is a compound of a following formula (15-11) as a compound of a formula (20-4).

 $[Y_{11}, Y_{12}, R_{38}, R_{39},$ aa, and bb are as aforementioned among a formula.]

returning using a reducing agent, after carrying out a condensation polymerization — the above—mentioned formula (15-1)

The high molecular compound which comes out and has a repeating unit shown can be obtained. [0138]

The high molecular compound of this invention,

Formula (21)

 $Y_1 - W - Y_2$

[W shows among a formula the repeating unit which has the thiophene sulfoxide structure corresponding to the above-mentioned U. Y_1 and Y_2 are as aforementioned.]

After coming out and carrying out the condensation polymerization of the compound shown, it can manufacture also by returning (method C).

The repeating unit W which has the thiophene structure corresponding to each U is as follows. [0139]

U

W

[0140]

For example, it is a compound of a following formula (15–12) as a compound of a formula (21–4).

式(15-12)

 $[Y_{11}, Y_{12}, R_{38}, R_{39}, aa, and bb are as aforementioned among a formula.]$

returning using a reducing agent, after carrying out a condensation polymerization — the above—mentioned formula (15–1)

The high molecular compound which comes out and has a repeating unit shown can be obtained. [0141]

In the manufacturing method of this invention, as a substituent in which a condensation polymerization is possible, A halogen atom, an alkyl sulfonate group, an aryl sulfonate group, An arylated alkyl sulfonate group, an ester-of-boric-acid group, a sulfonium methyl group, a phosphonium methyl group, a phosphonate methyl group, a mono- halogenation methyl group, a boric acid group, a formyl group, a cyano group, a vinyl group, etc. are raised.

[0142]

As an alkyl sulfonate group, they are illustrated by a methanesulfonate group, an ethane sulfonate group, trifluoro methanesulfonate group, etc., and here as an aryl sulfonate group, A benzene sulfonate group, a p-toluene sulfonate group, etc. are illustrated, and a benzyl sulfonate group etc. are illustrated as an aryl sulfonate group.

[0143]

The basis shown with a following formula is illustrated as an ester-of-boric-acid group.

Me shows a methyl group among a formula and Et shows an ethyl group.

[0144]

The basis shown with a following formula is illustrated as a sulfonium methyl group.

 $- CH_2S^+Me_2X^-, -CH_2S^+Ph_2X^-$

(X shows a halogen atom and Ph shows a phenyl group.)

[0145]

The basis shown with a following formula is illustrated as a phosphonium methyl group.

- CH₂P⁺Ph₃X⁻ (X shows a halogen atom.)

[0146]

The basis shown with a following formula is illustrated as a phosphonate methyl group.

- CH $_2$ PO(OR') $_2$ (X shows a halogen atom and R' shows an alkyl group, an aryl group, and an arylated alkyl group.)

[0147]

As a mono- halogenation methyl group, a methyl fluoride group, a methyl-chloride group, a methyl bromide group, and a methyl iodide group are illustrated.
[0148]

Although a substituent desirable as a substituent in which a condensation polymerization is possible changes with kinds of polymerization reaction, For example, when using zerovalent nickel complexes, such as a Yamamoto coupling reaction, a halogen atom, an alkyl sulfonate group, an aryl sulfonate group, or an arylated alkyl sulfonate group is mentioned. When using nickel catalysts, such as a Suzuki coupling reaction, or a palladium catalyst, an alkyl sulfonate group, a halogen atom, an ester-of-boric-acid group, a boric acid group, etc. are mentioned. [0149]

The compound which has a substituent used as repeating units other than a thiophene condensed ring unit in which two condensation polymerizations are possible is made to live together, and what is necessary is just to carry out a condensation polymerization, when the high molecular compound of this invention has repeating units other than a thiophene condensed ring unit.

[0150]

As a compound used as repeating units other than a thiophene condensed ring unit which has a substituent in which two condensation polymerizations are possible, the compound of above-mentioned formula (16) – (19) is illustrated. In addition to the compound shown by the above-mentioned formula (15), the condensation polymerization of the compound shown by either of following formula (16) – (19) is carried out.

Formula (16)

$$Y_3 - Ar_1 - Y_4$$

formula (17)

$$Y_5 - (A r_2 - X_1) - (A r_3 - Y_6)$$

formula (18)

$$Y_7 - Ar_4 - X_2 - Y_8$$

formula (19)

$$Y_9 - X_3 - Y_{10}$$

[Ar₁, Ar₂, Ar₃, Ar₄, ff, X ₁, X ₂, and X ₃ are the same as the above among a formula. Y₃, Y₄, Y₅, Y₆, Y₇, Y₈, Y₉, and Y₁₀ show the substituent in which a condensation polymerization is independently possible respectively.]

the unit shown by above-mentioned formula (1-1) - (1-5) - in addition, the high molecular compound which has one or more units of (3), (4), (5), or (6) in order can be manufactured. [0151]

It is a compound used as repeating units other than a thiophene condensed ring unit preferably shown with a following formula (22-1) as a compound which has a substituent in which two condensation polymerizations are possible.

$$Y_{25} \longrightarrow Ar_{6} \longrightarrow N \longrightarrow Ar_{7} \longrightarrow N \longrightarrow X Ar_{8} \longrightarrow Y_{26}$$

$$Ar_{9} \longrightarrow Ar_{10}$$

$$N \longrightarrow Ar_{11}$$

$$Ar_{12}$$

$$(22 - 1)$$

 $[Ar_6, Ar_7, Ar_8, Ar_9, Ar_{10}, Ar_{11}, Ar_{12}, x, and y are the same as the above among a formula. Y₂₅ and Y₂₆ show the substituent in which a condensation polymerization is independently possible$

respectively.]

It is a compound shown by a formula (22-2) still more preferably.

$$Y_{27} \xrightarrow{\left(\begin{array}{c} R_{50} \\ \\ \end{array}\right)_{hh}} X_{27} \xrightarrow{\left(\begin{array}{c} R_{51} \\ \\ \end{array}\right)_{ij}} Y_{28}$$

$$\left(\begin{array}{c} R_{52} \\ \\ \end{array}\right)_{jj}$$

$$\left(\begin{array}{c} R_{52} \\ \end{array}\right)_{jj}$$

[R_{50} , R_{51} , R_{52} , hh, ii, jj, and z are the same as the above among a formula. Y_{27} and Y_{28} show the substituent in which a condensation polymerization is independently possible respectively.] [0152]

It can be dissolved in an organic solvent by the manufacturing method of this invention if needed, for example, specifically, more than the melting point of an organic solvent can perform the compound used as a monomer which carries out two or more owners of the reactive substituent below in the boiling point using alkali or a suitable catalyst. For example, "ORUGA nick rear KUSHONZU (Organic Reactions)", the 14th volume, 270 – 490 pages, John Wiley And SANZU (John Wiley&Sons, Inc.), 1965 and "ORUGA nick synthesis (Organic Syntheses)" — collective — the 6th volume (Collective Volume VI), 407 – 411 pages, John Wiley And SANZU (John Wiley&Sons, Inc.), 1988, chemical A review (Chem.Rev.), the 95th volume, 2457 pages (1995), journal an OBUO luganot — metallic chemistry (J. Organomet.Chem.). Macromolecular [147 pages (1999)] the 576th volume Chemistry The publicly known method of a statement can be used for macromolecular symposium (Makromol.Chem., Macromol.Symp.), the 12th volume, 229 pages (1987), etc.

[0153]

In the manufacturing method of the high molecular compound of this invention, it can manufacture by using a known condensation reaction as a method of carrying out a condensation polymerization according to the substituent in which the condensation polymerization of the compound expressed with above-mentioned formula (14) - (22-2) is possible. When the high molecular compound of this invention generates a double bond in a condensation polymerization, the method of a statement is mentioned, for example to JP,5-202355,A. Namely, the compound which has a formyl group and the compound which has a phosphonium methyl group, Or the polymerization by the Wittig reaction of the compound which has a formyl group and a phosphonium methyl group, The polymerization by the Heck reaction of the compound which has a vinyl group, and the compound which has a halogen atom, The polycondensation according a mono- halogenation methyl group to two or the dehydrohalogenation method of a compound which it has two or more, The polycondensation according a sulfonium methyl group to two or the sulfonium salinity solution of a compound which it has two or more, Methods, such as a polymerization by the Knoevenagel reaction of the compound which has a formyl group, and the compound which has a cyano group, and methods, such as a polymerization according a formyl group to two or the McMurry reaction of a compound which it has two or more, are illustrated.

When the high molecular compound of this invention generates a triple bond to a main chain by a condensation polymerization, a Heck reaction can be used, for example.

[0154]

In generating neither a double bond nor a triple bond, For example, the method of polymerizing by a Suzuki coupling reaction from an applicable monomer, The method of polymerizing with

oxidizers, such as the method of polymerizing by a Grignard reaction, the method of polymerizing with nickel (0) complex, and FeCl₃, the method of carrying out oxidative polymerization electrochemically, or the method by disassembly of the intermediate polymers which have a suitable leaving group is illustrated.
[0155]

A polymerization according to a Wittig reaction among these, the polymerization by a Heck reaction, Since it is easy to carry out structure control, the method of polymerizing by the polymerization by a Knoevenagel reaction and a Suzuki coupling reaction, the method of polymerizing by a Grignard reaction, and the method of polymerizing by nickel-zero valent complex are preferred.

[0156]

In the manufacturing method of this invention, Y₁, Y₂, Y₃, Y₄, Y₅, Y₆, Y₇, Y₈, Y₉, Y₁₀, Y₁₁, and Y₁₂ independently, respectively A halogen atom, It is an alkyl sulfonate group, an aryl sulfonate group, or an arylated alkyl sulfonate group, and the manufacturing method which carries out a condensation polymerization under nickel–zero valent complex existence is preferred. As a raw material compound, a dihalogen–ized compound, a bis(alkyl sulfonate)compound, A bis (aryl sulfonate)compound, a bis(arylated alkyl sulfonate)compound, or a halogen alkyl sulfonate compound, A halogen aryl sulfonate compound, a halogen arylated alkyl sulfonate compound, An alkyl sulfonate aryl sulfonate compound, an alkyl sulfonate arylated alkyl sulfonate compound, and an aryl sulfonate arylated alkyl sulfonate compound, and an aryl sulfonate arylated alkyl sulfonate compound, and an aryl sulfonate arylated alkyl sulfonate compound are mentioned.

Y₁, Y₂, Y₃, Y₄, Y₅, Y₆, Y₇, Y₈, Y₉, Y₁₀, Y₁₁, and Y₁₂ independently in the manufacturing method of this invention, respectively A halogen atom, An alkyl sulfonate group, an aryl sulfonate group, an arylated alkyl sulfonate group, Are a boric acid group or an ester-of-boric-acid group, and The sum total (J) of the number of mols of a halogen atom, an alkyl sulfonate group, an aryl sulfonate group, and an arylated alkyl sulfonate group, The ratio of the sum total (K) of the number of mols of a boric acid group and an ester-of-boric-acid group is 1 (K/J is usually the range of 0.7-1.2) substantially, and the manufacturing method which carries out a condensation polymerization using a nickel catalyst or a palladium catalyst is preferred.

[0158]

As for the solvent to be used, although it changes as an organic solvent also with the compounds and reactions to be used, in order to inhibit a side reaction generally, it is preferred to fully perform deoxidation treatment and to advance a reaction by inert atmosphere—ization. It is preferred to perform dehydrating treatment similarly. However, in the case of the reaction in a 2 phase system with water like a Suzuki coupling reaction, it is not the limitation. [0159]

In order to make it react, alkali and a suitable catalyst are added suitably. What is necessary is just to choose these according to the reaction to be used. As for this alkali or a catalyst, what is fully dissolved in the solvent used for a reaction is preferred. As a method of mixing alkali or a catalyst, the method of adding alkali or the solution of a catalyst slowly, or adding reaction mixture slowly in alkali or the solution of a catalyst conversely is illustrated, stirring reaction mixture under the inert atmosphere of argon, nitrogen, etc.

Since the purity affects the performance of elements, such as a luminescent characteristic, when using the high molecular compound of this invention for polymers LED etc., it is preferred

to polymerize, after refining the monomer before a polymerization by methods, such as distillation, sublimation refining, and recrystallization. It is preferred after a polymerization to carry out purification processing of reprecipitation refining, judgment by chromatography, etc. [0161]

The compound shown by the above-mentioned formula (14) can manufacture the compound shown by the above-mentioned formula (20) or (21) by returning using a reducing agent. For example, The dibenzo thiophene derivative shown by the above-mentioned formula (15-1) can manufacture the compound shown with a following formula (15-11) by returning using a reducing agent.

$$Y_{11}$$
 Q Q Y_{12} Y_{12} $(R_{38})_{aa}$ $(R_{39})_{bb}$ $\overrightarrow{\mathbb{R}}(15-11)$

$[Y_{11}, Y_{12}, R_{38}, R_{39}, aa, and bb are as aforementioned among a formula.] [0162]$

Although not limited, especially as a reducing agent Titanium compounds, such as titanium trichloride, Silane compounds, such as trichlorosilane, hydrogenation aluminum, hydrogenation JI i-butylaluminum, Lithium aluminum hydride, hydrogenation trimethoxy aluminum lithium, Hydrogenation Tori t-butoxyaluminum lithium, hydrogenation aluminum sodium, Hydrogenation TORIETOKI sial minium sodium, hydrogenation bis(2-methoxyethoxy)aluminum sodium, Hydrogenation aluminium compounds, such as hydrogenation diethylaluminum sodium, Diborane, dichloroborane, 2,3-dimethyl- 2-butylborane, Bis-3-methyl-2-butylborane, JIISOPINO can phenylborane, Dicyclohexyl borane and 9 - bora -- diboranes, such as bicyclo[3.3.1] nonane,. A substitution borane compound, lithium borohydride, hydrogen cyanide-ized boron lithium, Boron hydride metallic compounds, such as hydrogenation triethylboron lithium, hydrogenation s-butyl boron lithium, hydrogenation t-butyl boron lithium, sodium borohydride, hydrogenation trimethoxy boron sodium, and hydrogen sulfide-ized boron sodium, And multicomputer systems, such as a tetrafluoroboric acid trimethyl oxonium boron hydride sodium series, a boron hydride sodium salt-ized cobalt system, and a methyl-hydrogen cyanide fluorosulfonate-ized boron sodium series, etc. are illustrated. A hydrogenation aluminium compound is preferred and especially lithium aluminum hydride is especially preferred.

[0163]

A reduction reaction can be carried out under existence of a solvent under the inert atmosphere of nitrogen, argon, etc. The temperature of a reaction has the desirable boiling point of -80 ** to a solvent.

[0164]

As a solvent, saturated hydrocarbon, such as pentane, hexane, heptane, octane, and cyclohexane, Unsaturated hydrocarbon, such as benzene, toluene, ethylbenzene, and xylene, A carbon tetrachloride, chloroform, dichloromethane, chlorobutane, bromobutane, Chloropentane, bromopentane, chlorohexane, bromohexane, Halogenation saturated hydrocarbon, such as chlorocyclohexane and bromocyclohexane, Halogenation unsaturated hydrocarbon, such as chlorobenzene, dichlorobenzene, and trichlorobenzene, Methanol, ethanol, propanol, isopropanol, butanol, Carboxylic acid, such as alcohols, such as t-butyl alcohol, formic acid, acetic acid, and propionic acid. Wood ether, diethylether, methyl-t-butyl ether, Ether, such as a tetrahydrofuran, tetrahydropyran, and dioxane, trimethylamine, triethylamine, N,N, and N — '— N'— tetramethylethylenediamine. They are illustrated by amide, such as amines, such as pyridine,

N.N-dimethylformamide, N,N-dimethylacetamide, a N,N-diethylacetamide, and N-methylmorpholineoxide, and A single solvent, Or these mixed solvents may be used. In these, ether is preferred and a tetrahydrofuran and diethylether are still more preferred.

[0165]

After quenching after a reaction with water and an organic solvent extracts it, for example, distilling off a solvent etc. can obtain it by the usual post-processing.

Isolation and refining of output can be performed by methods by chromatography, such as preparative isolation and recrystallization.

[0166]

Next, the use of the high molecular compound of this invention is explained.

By a solid state, the high molecular compound of this invention has fluorescence or phosphorescence, and it can be used for it as a polymers photogen (luminescent material of the amount of polymers). This high molecular compound has the outstanding electron transportation ability, and can use it conveniently as the charge of polymers LED material, or a charge transporting material. Polymers LED using this polymers photogen is a low voltage and highly efficient polymers LED which it is efficient and can be driven. Therefore, this polymers LED can be preferably used for devices, such as curved surface shape as the back light or the object for lighting of a liquid crystal display, a planate light source, a display device of a segment type, and a flat—panel display of a dot matrix.

The high molecular compound of this invention can be used also as charges of conductive thin film material, such as coloring matter for laser, a charge of organic solar cell material, an organic semiconductor for organic transistors, a conductive thin film, and an organic semiconductor thin film.

It can use also as a luminescent thin film material which emits fluorescence and phosphorescence.

[0167]

Next, polymers LED of this invention is explained.

Polymers LED of this invention has an organic layer in inter-electrode [which consists of the anode and the negative pole], and this organic layer contains the high molecular compound of this invention.

Although organic layers may be any, such as a luminous layer, an electron hole transporting bed, and an electron transport layer, it is preferred that an organic layer is a luminous layer. [0168]

The layer in which a luminous layer says the layer which has a function which emits light to, an electron hole transporting bed means here the layer which has the function to convey an electron hole, and an electron transport layer has here the function to convey an electron is said. An electron transport layer and an electron hole transporting bed are generically called a charge transport layer. A luminous layer, an electron hole transporting bed, and an electron transport layer may be used more than two-layer independently, respectively.

[0169]

When an organic layer is a luminous layer, the luminous layer which is an organic layer may include the hole transporting material, the electron transport material, or the luminescent material further. Here, a luminescent material puts the thing of the material in which fluorescence and/or phosphorescence are shown.

When mixing with the high molecular compound of this invention, and a hole transporting material, it is the whole mixture.

It receives, and it is alike and it is [the mixing ratio of a hole transporting material is 1wt% - 80wt%, and] 5wt% - 60wt% preferably. When mixing the polymer material and electron transport material of this invention, the mixing ratio of electron-transport-property material is 1wt% - 80wt% to the whole mixture, and it is 5wt% - 60wt% preferably. When mixing the high molecular compound and luminescent material of this invention, the mixing ratio of a luminescent material is 1wt% - 80wt% to the whole mixture, and it is 5wt% - 60wt% preferably. When mixing the high molecular compound, the luminescent material, hole transporting material, and/or electron transport material of this invention, the mixing ratio of a luminescent material is 1wt% - 50wt% to

the whole mixture, It is 5wt% - 40wt% preferably, a hole transporting material and an electron transport material are 1wt% - 50wt% in those sum totals, it is 5wt% - 40wt% preferably, and the content of the high molecular compound of this invention is 99wt% - 20wt%. [0170]

Although the hole transporting material, the electron–transport–property material, and the luminescent material to mix can use a publicly known low molecular weight compound, a triplet emission complex, or a high molecular compound, it is preferred to use a high molecular compound. As the hole transporting material, electron transport material, and luminescent material of a high molecular compound, WO99/13692, WO99/48160, GB2340304A, WO00/53656, WO01/19834, WO00/55927, GB2348316, WO00/46321, WO00/06665, WO99/54943, WO99/54385, US5777070, WO98/06773, WO97/05184, WO00/35987, WO00/53655, WO01/34722, WO99/24526, WO00/22027, WO00/22026, WO98/27136, US573636, WO98/21262, US5741921, WO97/09394, WO96/29356, WO96/10617, EP0707020, WO95/07955, JP,2001–181618,A, JP,2001–123156,A, JP,2001–3045,A, JP,2000–351967,A, JP,2000–303066,A, JP,2000–299189,A, JP,2000–252065,A, JP,2000–136379,A, JP,2000–104057,A, JP,2000–80167,A, Polyful Oren currently indicated by JP,10–324870,A, JP,10–114891,A, JP,9–111233,A, JP,9–45478,A, etc., The polymer (**) of the derivative and a copolymer, polyarylene, its derivative and a copolymer, polyarylene vinylene, its derivative and a copolymer, polyarylene vinylene, its derivative and its derivative is illustrated.

Consider it as the fluorescence material of a low molecular weight compound, and then, for example A naphthalene derivative, anthracene, or its derivative, Perylene or its derivative, a poly methine system, a xanthene series, a coumarin series, Coloring matter, such as a cyanine system, 8-hydroxyquinoline or the metal complex of the derivative, aromatic amine, a tetraphenylcyclopentadiene, its derivative, tetraphenylbutadiene, or its derivative can be used. Specifically, it is usable in publicly known things, such as what is indicated, for example in JP,57-51781,A and a 59-194393 gazette.

[0171]

As a triplet emission complex, Ir(ppy)3 which uses iridium as a central metal, Btp₂Ir (acac), PtOEP which uses platinum as a central metal, Eu(TTA)3phen which uses europium as a central metal, etc. are mentioned, for example.
[0172]

[0174]

$$\begin{array}{c|c} C_2H_5 & C_2H_5 \\ \hline \end{array} \qquad \begin{array}{c} PtOEP \\ \hline C_2H_5 & C_2H_5 \\ \hline \end{array}$$

[0175]

As a triplet emission complex, specifically, for example Nature (1998), 395, 151, and Appl. Phys. Lett. (1999), 75 (1), 4, and Proc. SPIE-Int. Soc. Opt. Eng. (2001), 4105 (Organic Light-Emitting Materials andDevicesIV), 119, J. Am. Chem. Soc. (2001), 123, 4304, and Appl. Phys. Lett. (1997), 71 (18), 2596, and Syn. Met. (1998), It is indicated to 94 (1), 103, Syn. Met. (1999), 99 (2), 1361, Adv. Mater. (1999), 11 (10), 852, Jpn.J.Appl.Phys., 34, 1883 (1995), etc. [0176]

If what has only the structure shown by a formula (1-4) is used as a high molecular compound mixed with a triplet emission complex, since it can use phosphorescence and the quantum efficiency of luminescence can be raised, it is desirable.

[0177]

The constituent of this invention contains the high molecular compound of at least one kind of material chosen from a hole transporting material, an electron transport material, and a luminescent material, and this invention, and it can be used for it as a luminescent material or a charge transporting material.

Although what is necessary is just to decide according to a use, when it is a use of a luminescent material, also in the above-mentioned luminous layer, the same content ratio of the content ratio of the high molecular compound of at least one kind of material chosen from the hole transporting material, an electron transport material, and a luminescent material and this invention is preferred.

[0178]

As thickness of the luminous layer which polymers LED of this invention has, Although what is necessary is for an optimum value to change with materials to be used, and just to choose so that it may become driver voltage and a value with moderate luminous efficiency, for example from 1 nm, it is 1 micrometer, and is 2 nm - 500 nm preferably, and they are 5 nm - 200 nm still more preferably.

[0179]

As a formation method of a luminous layer, the method by the membrane formation from a solution is illustrated, for example. As a method for film deposition from a solution, a spin coat method, casting method, The applying methods, such as the micro gravure coating method, the gravure coating method, the bar coat method, the roll coat method, the wire bar coat method, a dip coating method, a spray coating method, screen printing, flexo print processes, offset printing, and the ink jet printing method, can be used. pattern formation and a multicolor ** part injury — print processes, such as screen printing, flexo print processes, offset printing, and the

ink jet printing method, are preferred at the point of being easy. [0180]

As an ink composition used by print processes etc., the high molecular compound of at least one kind of this invention should just contain, and additive agents, such as a hole transporting material, an electron transport material, a luminescent material, a solvent, and stabilizer, may be included in addition to the high molecular compound of this invention.

The percentage of the high molecular compound of this invention in this ink composition is usually 20wt% - 100wt% to the full weight of the constituent except a solvent, and is 40wt% - 100wt% preferably.

The percentage of a solvent in case a solvent is contained in an ink composition is 1wt% - 99.9wt% to the full weight of a constituent, is 60wt% - 99.5wt% preferably, and is 80wt% - 99.0wt% still more preferably.

Although the viscosity of an ink composition changes with print processes, in order to prevent the loading at the time of the regurgitation, and a flight bend, to the that case in which the inside of ink compositions, such as the ink jet printing method, goes via a discharging device, it is preferred that viscosity is the range of 1 - 20 mPa-s in 25 **.

[0181]

Although there is no restriction in particular as a solvent used as an ink composition, the dissolution or the thing which can be distributed uniformly is preferred in materials other than the solvent which constitutes this ink composition. When meltable [to a nonpolar solvent] in the material which constitutes this ink composition, As this solvent, chlorine—based solvents, such as chloroform, a methylene chloride, and a dichloroethane, Ester solvent, such as ketone solvent, such as aromatic hydrocarbon system solvents, such as ether system solvents, such as a tetrahydrofuran, toluene, and xylene, acetone, and methyl ethyl ketone, ethyl acetate, butyl acetate, and ethyl Cellosolve acetate, is illustrated.

[0182] Between polymers LED, the anode, and the luminous layer which provided the electron transport layer between the negative pole and a luminous layer as polymers LED of this invention, Polymers LED etc. which provided the electron transport layer between polymers LED, the negative pole, and the luminous layer which provided the electron hole transporting bed, and provided the electron hole transporting bed in it between the anode and a luminous layer are mentioned.

[0183]

For example, specifically, the following structures of a-d are illustrated.

- a) The anode / luminous layer / negative pole
- b) The anode / electron hole transporting bed / luminous layer / negative pole
- c) The anode / luminous layer / electron transport layer / negative pole
- d) The anode / electron hole transporting bed / luminous layer / electron transport layer / negative pole

(Here, it is shown that each class adjoins and / is laminated.) It is below the same. [0184]

When polymers LED of this invention has an electron hole transporting bed, as a hole transporting material used, A polyvinyl carbazole or its derivative, polysilane, or its derivative, The polysiloxane derivative, pyrazoline derivative which have aromatic amine in a side chain or a main chain, An arylamine derivative, a stilbene derivative, a triphenyl diamine derivative, Poly aniline or its derivative, a polythiophene or its derivative, polypyrrole or its derivative, poly (p-phenylenevinylene), its derivative, poly (2,5-thienylene vinylene), or its derivative is illustrated. [0185]

As this hole transporting material, specifically JP,63-70257,A, What is indicated in a 63-175860 gazette, JP,2-135359,A, the 2-135361 gazette, the 2-209988 gazette, the 3-37992 gazette, and the 3-152184 gazette is illustrated.

[0186]

In these, as a hole transporting material used for an electron hole transporting bed, a polyvinyl carbazole or its derivative, The polysiloxane derivative which has an aromatic amine compound

group in polysilane or its derivative, a side chain, or a main chain, Poly aniline or its derivative, a polythiophene, or its derivative, Polymers hole transporting materials, such as poly (p-phenylenevinylene), its derivative, poly (2,5-thienylene vinylene), or its derivative, are preferred, It is a polysiloxane derivative which has aromatic amine still more preferably in a polyvinyl carbazole or its derivative, polysilane or its derivative, a side chain, or a main chain. [0187]

As a hole transporting material of a low molecular weight compound, a pyrazoline derivative, an arylamine derivative, a stilbene derivative, and a triphenyl diamine derivative are illustrated. It is preferred to distribute a high polymer binder in the case of a low-molecular hole transporting material, and to use for it.

[0188]

What has the absorption what does not check charge transport to a degree very much is preferred as a high polymer binder to mix, and not strong to visible light is used suitably. As this high polymer binder, poly (N-vinylcarbazole), poly aniline, or its derivative, A polythiophene or its derivative, poly (p-phenylenevinylene), or its derivative, Poly (2,5-thienylene vinylene) or its derivative, polycarbonate, polyacrylate, polymethyl acrylate, polymethylmethacrylate, polystyrene, polyvinyl chloride, a polysiloxane, etc. are illustrated.

A polyvinyl carbazole or its derivative is obtained, for example from a vinyl monomer by cationic polymerization or a radical polymerization.

[0190]

[0189]

As polysilane or its derivative, a compound given in the 89th volume of a chemical review (Chem.Rev.), 1359 pages (1989), and the British patent GB No. 2300196 public presentation specification etc. are illustrated. Although a synthesizing method can also use the method of a statement for these, especially the Kipping method is used suitably.

[0191]

[0194]

[0195]

That to which a polysiloxane or its derivative has the structure of the above-mentioned low molecule hole transporting material in a side chain or a main chain since there is almost no electron hole transportability in siloxane skeletal structure is used suitably. What has especially the aromatic amine of electron hole transportability in a side chain or a main chain is illustrated. [0192]

Although there is no restriction in the method of membrane formation of an electron hole transporting bed, in a low molecule hole transporting material, the method by the membrane formation from a mixed solution with a high polymer binder is illustrated. In a polymers hole transporting material, the method by the membrane formation from a solution is illustrated. [0193]

As a solvent used for the membrane formation from a solution, if a hole transporting material is dissolved, there will be no restriction in particular. As this solvent, chlorine—based solvents, such as chloroform, a methylene chloride, and a dichloroethane, Ester solvent, such as ketone solvent, such as aromatic hydrocarbon system solvents, such as ether system solvents, such as a tetrahydrofuran, toluene, and xylene, acetone, and methyl ethyl ketone, ethyl acetate, butyl acetate, and ethyl Cellosolve acetate, is illustrated.

As a method for film deposition from a solution, a spin coat method from a solution, casting method, The applying methods, such as the micro gravure coating method, the gravure coating method, the bar coat method, the roll coat method, the wire bar coat method, a dip coating method, a spray coating method, screen printing, flexo print processes, offset printing, and the ink jet printing method, can be used.

Although what is necessary is for an optimum value to change as thickness of an electron hole transporting bed with materials to be used, and just to choose so that it may become driver voltage and a value with moderate luminous efficiency, thickness which a pinhole does not generate at least is required, and if not much thick, the driver voltage of an element becomes high and is not preferred. Therefore, as thickness of this electron hole transporting bed, for

example from 1 nm, it is 1 micrometer, and is 2 nm - 500 nm preferably, and they are 5 nm - 200 nm still more preferably.

[0196]

When polymers LED of this invention has an electron transport layer, a publicly known thing can be used as an electron transport material used, An oxadiazole derivative, anthra quinodimethane, or its derivative, Benzoquinone or its derivative, a naphthoquinone, or its derivative, Anthraquinone or its derivative, tetracyano ANSURA quinodimethane, or its derivative, A fluorenone derivative, diphenyldicyanoethylene, or its derivative, A diphenoquinone derivative, 8-hydroxyquinoline or the metal complex of the derivative, polyquinoline or its derivative, polyquinoxaline or its derivative, Polyful Oren, or its derivative is illustrated. [0197]

Specifically, what is indicated in JP,63-70257,A, a 63-175860 gazette, JP,2-135359,A, the 2-135361 gazette, the 2-209988 gazette, the 3-37992 gazette, and the 3-152184 gazette is illustrated.

[0198]

Among these An oxadiazole derivative, benzoquinone, or its derivative, Anthraquinone, its derivative, 8-hydroxyquinoline, or the metal complex of the derivative, Polyquinoline or its derivative, polyquinoxaline, or its derivative, Polyful Oren or its derivative is preferred, and 2-(4-biphenylyl)-5-(4-t-buthylphenyl)-1,3,4-oxadiazole, benzoquinone, anthraquinone, tris(eight quinolinol) aluminum, and polyquinoline are still more preferred.
[0199]

Although there is no restriction in particular as a method of forming an electron transport layer, in a low molecule electron transport material, the method according [the method by the membrane formation from the vacuum deposition method, solution, or molten state from powder] to the membrane formation from a solution or a molten state is illustrated with a polymers electron transport material, respectively. The above-mentioned high polymer binder may be used together at the time of the membrane formation from a solution or a molten state. [0200]

As a solvent used for the membrane formation from a solution, if an electron transport material and/or a high polymer binder are dissolved, there will be no restriction in particular. As this solvent, chlorine-based solvents, such as chloroform, a methylene chloride, and a dichloroethane, Ester solvent, such as ketone solvent, such as aromatic hydrocarbon system solvents, such as ether system solvents, such as a tetrahydrofuran, toluene, and xylene, acetone, and methyl ethyl ketone, ethyl acetate, butyl acetate, and ethyl Cellosolve acetate, is illustrated.
[0201]

As a method for film deposition from a solution or a molten state, A spin coat method, casting method, the micro gravure coating method, the gravure coating method, The applying methods, such as the bar coat method, the roll coat method, the wire bar coat method, a dip coating method, a spray coating method, screen printing, flexo print processes, offset printing, and the ink jet printing method, can be used.

[0202]

Although what is necessary is for an optimum value to change as thickness of an electron transport layer with materials to be used, and just to choose so that it may become driver voltage and a value with moderate luminous efficiency, thickness which a pinhole does not generate at least is required, and if not much thick, the driver voltage of an element becomes high and is not preferred. Therefore, as thickness of this electron transport layer, for example from 1 nm, it is 1 micrometer, and is 2 nm - 500 nm preferably, and they are 5 nm - 200 nm still more preferably.

[0203]

Generally what has the function to improve the electric charge injection efficiency from an electrode among the charge transport layers which adjoined the electrode and were provided, and has the effect of dropping the driver voltage of an element may be called especially an electric charge pouring layer (a hole injection layer, an electronic injection layer). [0204]

Furthermore, for an improvement of the improvement in adhesion with an electrode, and electric charge pouring from an electrode, an electrode may be adjoined, and the aforementioned electric charge pouring layer or the insulating layer of 2 nm or less of thickness may be provided, and a thin buffer layer may be inserted in the interface of a charge transport layer or a luminous layer for the improvement in adhesion of an interface, mixed prevention, etc.

About the turn of the layer to laminate, a number, and the thickness of each class, luminous efficiency and an element life can be taken into consideration, and it can use suitably. [0205]

In this invention, polymers LED which adjoined the negative pole and provided the electric charge pouring layer as polymers LED which provided the electric charge pouring layer (an electronic injection layer, a hole injection layer), and polymers LED which adjoined the anode and provided the electric charge pouring layer are mentioned.

For example, specifically, the following structures of e-p are mentioned.

- e) The anode / electric charge pouring layer / luminous layer / negative pole
- f) The anode / luminous layer / electric charge pouring layer / negative pole
- g) The anode / electric charge pouring layer / luminous layer / electric charge pouring layer / negative pole
- h) The anode / electric charge pouring layer / electron hole transporting bed / luminous layer / negative pole
- i) The anode / electron hole transporting bed / luminous layer / electric charge pouring layer / negative pole
- j) The anode / electric charge pouring layer / electron hole transporting bed / luminous layer / electric charge pouring layer / negative pole
- k) The anode / electric charge pouring layer / luminous layer / electron transport layer / negative pole
- I) The anode / luminous layer / electron transport layer / electric charge pouring layer / negative pole
- m) The anode / electric charge pouring layer / luminous layer / electron transport layer / electric charge pouring layer / negative pole
- n) The anode / electric charge pouring layer / electron hole transporting bed / luminous layer / electron transport layer / negative pole
- o) The anode / electron hole transporting bed / luminous layer / electron transport layer / electric charge pouring layer / negative pole
- p) The anode / electric charge pouring layer / electron hole transporting bed / luminous layer / electron transport layer / electric charge pouring layer / negative pole [0206]

As a concrete example of an electric charge pouring layer, it is provided between the layer, and the anode and the electron hole transporting bed containing a conductive polymer, It is provided between a layer, and the negative pole and the electron transport layer containing the material which has the ionization potential of the middle value of an anode material and the hole transporting material included in an electron hole transporting bed, and the layer containing the material which has the electron affinity of the middle value of a cathode material and the electron transport material included in an electron transport layer are illustrated.

[0207]

In the case of the included layer, the above-mentioned electric charge pouring layer a conductive polymer the electrical conductivity of this conductive polymer, It is preferred that more than 10^{-5} S/cm is below 10^{-3} , in order to make the leakage current between emission pixels small, below 10^{-2} is [more than 10^{-5} S/cm] more preferred, and below 10^{-1} is [more than 10^{-5} S/cm] still more preferred.

[0208]

In the case of the included layer, the above-mentioned electric charge pouring layer a conductive polymer the electrical conductivity of this conductive polymer, In order it is preferred that more than 10⁻⁵S/cm is below 10 ³S/cm and to make the leakage current between emission

pixels small, Below 10 2 S/cm is [more than 10^{-5} S/cm] more preferred, and below 10 1 S/cm is [more than 10^{-5} S/cm] still more preferred.

Usually, in order for below 10 3 to carry out [more than 10^{-5} S/cm] the electrical conductivity of this conductive polymer, optimum dose of ion is doped to this conductive polymer. [0209]

If the kind of ion to dope is a hole injection layer and they are an anion and an electronic injection layer, it is a cation. As an example of an anion, polystyrene sulfonate ion, alkylbenzene-sulfonic-acid ion, camphor sulfonic acid ion, etc. are illustrated, and a lithium ion, sodium ion, potassium ion, tetrabuthyl ammonium ion, etc. are illustrated as an example of a cation. As thickness of an electric charge pouring layer, it is 1 nm - 100 nm, for example, and 2 nm - 50 nm are preferred.

[0210]

What is necessary is just to choose suitably the material used for an electric charge pouring layer by a relation with the material of an electrode or the adjoining layer, Poly aniline and its derivative, a polythiophene, and its derivative, Polypyrrole and its derivative, polyphenylene vinylene, and its derivative, Conductive polymers, such as poly thienylene vinylene and its derivative, polyquinoline and its derivative, polyquinoxaline and its derivative, and a polymer that includes aromatic amine structure in a main chain or a side chain, metal phthalocyanines (copper phthalocyanine etc.), carbon, etc. are illustrated.

The insulating layer of 2 nm or less of thickness has a function which makes electric charge pouring easy. As a material of the above-mentioned insulating layer, metal fluoride, a metallic oxide, an organic insulating material, etc. are mentioned. Polymers LED which adjoined the negative pole and provided the insulating layer of 2 nm or less of thickness as polymers LED which provided the insulating layer of 2 nm or less of thickness, and polymers LED which adjoined the anode and provided the insulating layer of 2 nm or less of thickness are mentioned. [0212]

Concrete for example, the structure of following q-ab is mentioned.

- q) The insulating layer / luminous layer / negative pole of 2 nm or less of the anode / thickness
- r) The insulating layer/negative pole of 2 nm or less of the anode / luminous layer / thickness
- s) The insulating layer/negative pole of 2 nm or less of the insulating layer / luminous layer / thickness of 2 nm or less of the anode / thickness
- t) The insulating layer / electron hole transporting bed / luminous layer / negative pole of 2 nm or less of the anode / thickness
- u) The insulating layer/negative pole of 2 nm or less of the anode / electron hole transporting bed / luminous layer / thickness
- v) The insulating layer/negative pole of 2 nm or less of the insulating layer / electron hole transporting bed / luminous layer / thickness of 2 nm or less of the anode / thickness
- w) The insulating layer / luminous layer / electron transport layer / negative pole of 2 nm or less of the anode / thickness
- x) The insulating layer/negative pole of 2 nm or less of the anode / luminous layer / electron transport layer / thickness
- y) The insulating layer/negative pole of 2 nm or less of the insulating layer / luminous layer / electron transport layer / thickness of 2 nm or less of the anode / thickness
- z) The insulating layer / electron hole transporting bed / luminous layer / electron transport layer / negative pole of 2 nm or less of the anode / thickness
- aa) The insulating layer/negative pole of 2 nm or less of the insulating layer / electron hole transporting bed / luminous layer / electron transport layer / thickness of 2 nm or less of the insulating layer / negative pole ab anode / thickness of 2 nm or less of the anode / electron hole transporting bed / luminous layer / electron transport layer / thickness [0213]

When the substrate which forms polymers LED of this invention forms an electrode and forms the layer of an organic matter, it does not change, and glass, a plastic, a high polymer film, a

silicon substrate, etc. should just be illustrated. It is preferred that an electrode opposite in the case of an opaque substrate is transparent or translucent.
[0214]

Usually, at least one side of the anode and the negative pole which polymers LED of this invention has is transparent or translucent. It is preferred that the anode side is transparent or translucent.

As a material of this anode, a conductive metal oxide film, a translucent metal thin film, etc. are used. Indium tin oxide (ITO) which is specifically indium oxide, a zinc oxide, tin oxide, and those complexes, The films (NESA etc.) created using the electrically conductive glass which consists of indium, zinc, oxide, etc., gold and platinum, silver, copper, etc. are used, and ITO, indium, zinc and oxide, and the tin oxide are preferred. As a manufacturing method, a vacuum deposition method, sputtering process, the ion plating method, plating, etc. are mentioned. Organic transparent conducting films, such as poly aniline or its derivative, a polythiophene, or its derivative, may be used as this anode.

Although the thickness of the anode can be suitably chosen in consideration of the permeability of light, and electrical conductivity, for example from 10 nm, it is 10 micrometers, is 20 nm - 1 micrometer preferably, and is 50 nm - 500 nm still more preferably.

On the anode, in order to make electric charge pouring easy, the layer of 2 nm or less of average thickness which consists of the layer which consists of a phthalocyanine derivative, a conductive polymer, carbon, etc. or a metallic oxide and metal fluoride, an organic insulating material, etc. may be provided.

[0215]

As a material of the negative pole used by polymers LED of this invention, a small material of a work function is preferred. For example, lithium, sodium, potassium, a rubidium, caesium, Beryllium, magnesium, calcium, strontium, barium, Aluminum, a scandium, vanadium, zinc, yttrium, indium, In [those] metal, such as cerium, samarium, europium, a terbium, and an ytterbium, in [those] two or more alloys One or more. One or more alloys, graphite, or intercalated graphite etc. is used among gold, silver, platinum, copper, manganese, titanium, cobalt, nickel, tungsten, and tin. As an example of an alloy, a magnesium silver alloy, a magnesium indium alloy, A magnesium aluminum alloy, an indium silver alloy, a lithium aluminum alloy, a lithium Magnesium alloy, a lithium indium alloy, a calcium aluminum alloy, etc. are mentioned. It is good also considering the negative pole as a laminated structure more than two-layer.

Although the thickness of the negative pole can be suitably chosen in consideration of electrical conductivity or endurance, for example from 10 nm, it is 10 micrometers, is 20 nm - 1 micrometer preferably, and is 50 nm - 500 nm still more preferably.

[0216]

As a manufacturing method of the negative pole, a vacuum deposition method, sputtering process, the laminating method that bonds a metal thin film by thermo-compression, etc. are used. The layer of 2 nm or less of average thickness which consists of the layer which consists of conductive polymers or a metallic oxide and metal fluoride, an organic insulating material, etc. could be provided between the negative pole and an organic layer, and it may equip with the protective layer which protects this polymers LED after negative pole production. In order to use this polymers LED stably over a long period of time and to protect an element from the exterior, it is preferred to equip with a protective layer and/or a protective cover.

[0217]

As this protective layer, a high molecular compound, a metallic oxide, metal fluoride, metallic boride, etc. can be used. As a protective cover, a glass plate, the plastic sheet which performed low coefficient—of—water—permeability processing to the surface, etc. can be used, and the method of pasting this covering together to an element substrate and sealing it by thermal effect resin or photo—curing resin, is used suitably. If space is maintained using a spacer, it is easy for an element to prevent that of crack ****. If inertness gas like nitrogen or argon is enclosed with this space, oxidation of the negative pole can be prevented and it will become easy by installing driers, such as barium oxide, in this space further to control that the moisture to which it stuck by the manufacturing process gives TAMEJI to an element. It is [among these] preferred to

take any one or more policies.

T02187

Polymers LED of this invention can be used as a back light of the source of sheet-like light, a segment display, a dot matrix display, and a liquid crystal display.

What is necessary is just to arrange so that the anodes and the negative poles of surface state may overlap in order to obtain luminescence of surface state using polymers LED of this invention. How to install the mask which provided the window of pattern state in the surface of the light emitting device of said surface state in order to obtain luminescence of pattern state, There is the method of forming the electrode of either one of the method of forming the organic layer of a nonluminescent part extremely thickly, and making it nonluminescent substantially, the anode or the negative pole and both in pattern state. The display device of the segment type which can display a number, a character, an easy sign, etc. is obtained by forming a pattern by ones of these methods, and arranging so that On/OFF [some electrodes] independently. What is necessary is just to arrange so that the anode and the negative pole may be formed in stripe shape and it may intersect perpendicularly in order [both] to consider it as a dot-matrix element. A partial colored presentation and a multicolor display are attained by the method of distinguishing by different color the polymeric fluorescent substance in which the luminescent color of two or more kinds differs with, and the method of using a light filter or a fluorescence conversion filter. A passive drive is also possible and a dot-matrix element may carry out an active drive combining TFT etc. These display devices can be used as displays, such as a view finder of a computer, television, a personal digital assistant, a cellular phone, car navigation, and a video camera.

[0219]

It can be conveniently used for the light emitting device of said surface state with a spontaneous light thin shape as the source of sheet-like light for the back lights of a liquid crystal display, or a light source for lighting of surface state. If a flexible substrate is used, it can be used also as curved surface shape light source and display.

[0220]

[Example]

Hereafter, in order to explain this invention still in detail, an example is shown, but this invention is not limited to these.

Here, about the number average molecular weight, the number average molecular weight of polystyrene conversion was calculated with gel permeation chromatography (GPC) by using chloroform as a solvent.

[0221]

The synthetic example 1 (composition of compound A)

Compound A

After putting 7 g of 2,8-dibromo dibenzo thiophenes, and THF 280ml into a 1-l. 4 mouth flask under the inert atmosphere and agitating and melting at a room temperature, it cooled to -78 **. n-butyl lithium 29 ml (1.6-mol hexane solution) was dropped. It agitates after the end of dropping for 2 hours, with temperature held, and is a trimethoxy boron acid. 13 g was dropped. It returned to the room temperature slowly after the end of dropping. The churning back was checked at the room temperature for 3 hours, and disappearance of the raw material was checked by TLC. 5% sulfuric acid 100 ml was added, the reaction was terminated and it agitated at the room temperature for 12 hours. Water was added and washed and the organic layer was extracted. 30% hydrogen peroxide solution after replacing a solvent by ethyl acetate 5 ml was added and it agitated at 40 ** for 5 hours. It is a brown solid by extracting an organic layer after that, afterwashing drying in ammonium iron(II) sulfate solution 10%, and removing a solvent. 4.43 g was

obtained. By-products, such as a dimer, were also generated from liquid-chromatography-mass-spectrometry measurement, and the purity of compound A was 77% (LC side 100).

MS(APCI (-)): (M-H)⁻215

[0222]

The synthetic example 2 (composition of the compound B)

Compound B

It is compound A to a 200-ml three-neck flask under an inert atmosphere. 4.43-g and 25.1 g of n-octyl bromide, potassium carbonate 12.5 g (23.5mmol) is put in and it is methyl isobutyl ketone as a solvent. 50 ml was added and heating flowing back was carried out at 125 ** for 6 hours. After ending reaction, except for the solvent, it dissociated, the organic layer was extracted and it washed twice with water further with chloroform and water. The 8.49 g (197% of LC side, 94% of yield) compound B was obtained after desiccation with anhydrous sodium sulfate by refining with a silica gel column (developing solvent: toluene/cyclohexane =1/10).

 1 H-NMR (300 MHz/CDCl₃):

delta 0.91 (t, 6H), 1.31-1.90 (m, 24H), 4.08 (t, 4H), 7.07 (dd, 2H), 7.55 (d, 2H), 7.68 (d, 2H) [0223]

The synthetic example 3 (composition of the compound C)

Compound C

They are compound B 6.67g and acetic acid to a 100-ml three-neck flask. 40 ml was put in and temperature up was carried out to the bus temperature of 140 ** by the oil bath. Then, 30% hydrogen peroxide solution After adding 13 ml from a condenser tube and agitating it strongly for 1 hour, it flowed into 180 ml of chilled water, and the reaction was terminated. The 6.96 g (190% of LC side, 97% of yield) compound C was obtained by removing the solvent after extraction and desiccation under chloroform.

 1 H-NMR (300 MHz/CDCl₃) :

delta 0.90 (t, 6H), 1.26-1.87 (m, 24H), 4.06 (t, 4H), 7.19 (dd, 2H), 7.69 (d, 2H), 7.84 (d, 2H)

MS(APCI (+)): (M+H)+473

[0224]

The synthetic example 4 (composition of the compound D)

Compound D

They are compound C 3.96g and acetic acid/chloroform =1:1 mixed liquor to a bottom of inert atmosphere 200-ml 4 mouth flask. 15 ml was added and it was made to agitate and dissolve at 70 **. Then, bromine It is the above-mentioned solvent about 6.02 g. In addition, it agitated for 3

hours to 3 ml. Sodium subsulfite solution was added and unreacted bromine was removed, and with chloroform and water, the organic layer was extracted [separation and] and it dried. The 4.46 g (198% of LC side, 84% of yield) compound D was obtained by removing a solvent and refining with a silica gel column (developing solvent: chloroform/hexane =1/4).

¹H-NMR (300 MHz/CDCl₃) :

delta 0.95 (t, 6H), 1.30-1.99 (m, 24H), 4.19 (t, 4H), 7.04 (s, 2H), 7.89 (s, 2H)

MS(FD+) M+630

[0225]

Example 1 (composition of compound E)

Compound E

the bottom 200-ml three-neck flask of an inert atmosphere — compound D 3.9g and diethylether putting in 50 ml — up to 40 ** — temperature up — it agitated. Lithium aluminum hydride A little 1.17 g was added every and it was made to react for 5 hours. By adding a little water every, superfluous lithium aluminum hydride is disassembled and it is 36% chloride. It washed at 5.7 ml. It dried after extracting separation and an organic layer with chloroform and water. By refining with a silica gel column (developing solvent: chloroform/hexane =1/5), 1.8 g (199% of LC side, 49% of yield) of compound E was obtained.

 1 H-NMR (300 MHz/CDCl₃):

delta 0.90 (t, 6H), 1.26-1.97 (m, 24H), 4.15 (t, 4H), 7.45 (s, 2H), 7.94 (s, 2H)

MS(FD⁺) M⁺598

[0226]

MS (APCI (+)) -- according to the law, the peak was detected by 615 and 598.

[0227]

Example 2

Composition of the high molecular compound 1>

Compound E 352 mg and 2,2'-bipyridyl After dissolving in tetrahydrofuran 20mL which dried 274 mg, bubbling was carried out with nitrogen and the nitrogen purge of the inside of a system was carried out. In the bottom of a nitrogen atmosphere, it is bis(1, 5-cyclo-octadiene)nickel (0) [nickel(COD) 2] to this solution. Temperature up was carried out and it was made to react to 60

** in addition for 3 hours 500 mg. After cooling this reaction mixture to a room temperature (about 25 **) after a reaction, being dropped into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution and stirring for 1 hour, reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 30 ml of toluene. Then, it stirred for 1 hour, 30 ml of 1N chloride was added, the water layer removed, 30 ml of ammonia solutions were added to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at 200 ml of methanol, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in 30 ml of toluene. Then, it refined through the alumina column (the amount of alumina of 5g), the collected toluene solution was dropped at 250 ml of methanol, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained polymer was 46 mg.

This polymer is called the high molecular compound 1.

The average molecular weights of polystyrene conversion of the high molecular compound 1 were Mn= 2.1×10^{-4} and Mw= 8.1×10^{-4} . [0228]

Example 3

Composition of the high molecular compound 2>

Compound E 253 mg and N,N'-bis(4-bromophenyl)-N,N'-bis(4-n-buthylphenyl)-1,4phenylenediamine 125 mg and 2,2'-bipyridyl Tetrahydrofuran which dried 285 mg After dissolving in 20mL, Bubbling was carried out with nitrogen and the nitrogen purge of the inside of a system was carried out. In the bottom of a nitrogen atmosphere, it is bis(1, 5-cyclo-octadiene)nickel (0) {nickel(COD) ,} to this solution. 500 mg is added, and temperature up was carried out and it was made to react to 60 ** for 3 hours. This reaction mixture is cooled to a room temperature (about 25 **) after a reaction, and it is a 25% ammonia solution. Reduced pressure drying of the precipitate which deposited after being dropped into 120 ml of 10 ml / methanol / 50 ml of ionexchange-water mixed solution and stirring for 1 hour is filtered and carried out for 2 hours, and it is toluene. It was made to dissolve in 30 ml. Then, 1N chloride 30 ml is added, it stirs for 1 hour, a water layer removes, and it is a 4% ammonia solution to an organic layer. 30 ml was added, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at 200 ml of methanol, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in 30 ml of toluene. Then, it is methanol about the toluene solution refined and collected through the alumina column (the amount of alumina 5g). It was dropped at 250 ml, and stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. Yield of the obtained copolymer It was 127 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene and an amine derivative is 70:30. This copolymer is called the high molecular compound 2.

The average molecular weights of polystyrene conversion of the high molecular compound 2 were Mn= 2.3×10^{-4} and Mw= 5.8×10^{-4} .

[0229]

Example 4

Composition of the high molecular compound 3>

compound E 296 mg and a N,N-screw (4-bromophenyl) – N – ' – N' – diphenyl–1,4– phenylenediamine 144 mg and 2,2'-bipyridyl After dissolving in 24 ml of tetrahydrofurans which dried 330 mg, bubbling was carried out with nitrogen and the nitrogen purge of the inside of a system was carried out. In the bottom of a nitrogen atmosphere, it is bis(1, 5-cyclo-octadiene) nickel (0) {nickel(COD) } to this solution. Temperature up was carried out and it was made to

react to 60 ** in addition for 3 hours 600 mg. After cooling this reaction mixture to a room temperature (about 25 **) after a reaction, being dropped into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution and stirring for 1 hour, reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 30 ml of toluene. Then, it stirred for 1 hour, 30 ml of 1N chloride was added, the water layer removed, 30 ml of ammonia solutions were added to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at 200 ml of methanol, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in 30 ml of toluene. Then, it refined through the alumina column (the amount of alumina of 5g), the collected toluene solution was dropped at 250 ml of methanol, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 118 mg. From the preparation ratio of a monomer, the ratio of the repeating unit of a dibenzo thiophene and an amine derivative is 70:30 in a copolymer. This copolymer is called the high molecular compound 3.

The average molecular weights of polystyrene conversion of the high molecular compound 3 were Mn= 2.6×10^{-4} and Mw= 8.9×10^{-4} .

[0230] Example 5

Composition of the high molecular compound 4>

Compound E 6450 mg and 2070 mg of N,N-bis(4-bromophenyl)-N-(4-(1-methylbutyl) phenyl) amine, And 2,2'-bipyridyl In the bottom of the nitrogen atmosphere after dissolving in drying tetrahydrofuran 400mL beforehand deaerated with argon gas after putting 5500 mg into the flask and carrying out the nitrogen purge of the inside of a system, To this solution, it is bis(1, 5cyclo-octadiene)nickel (0) {nickel(COD) ₂}. Temperature up was carried out and it was made to react to 60 ** in addition for 3 hours 10000 mg. This reaction mixture is cooled to a room temperature after a reaction, and after filling reaction mixture with 100 ml of 500 ml of 100 ml of 25% ammonia solutions / methanol / ion exchange water and stirring it for 1 hour, reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 40 ml of toluene. The water layer was removed, after adding 1N chloride 40mL, stirring for 1 hour, having removed the water layer, adding ammonia solution 40mL to the organic layer 3% and stirring for 1 hour. The organic layer which 150 ml of ion exchange water furthermore washed, and was washed to methanol 100mL was poured out, and it stirred for 1 hour. Reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in toluene 40mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 200mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 4000 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene derivative and an amine derivative is 70:30.

This copolymer is called the high molecular compound 4.

The number average molecular weight of polystyrene conversion of the high molecular compound 4 was Mn=4.8x10 ⁴, and weight average molecular weight was Mw=5.3x10 ⁵. [0231]

Example 6

Composition of the high molecular compound 5>

Compound E 400 mg, N,N'-bis(4-bromophenyl)-N,N'-bis(3-methylphenyl)diphenylbenzidine After teaching 440 mg and 2, and 510 mg of 2'-bipyridyls to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 40 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 1000 mg of bis (1,5-cyclo-octadiene)nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 79 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene derivative and an amine derivative is 50:50.

This copolymer is called the high molecular compound 5.

The number average molecular weight of polystyrene conversion of the high molecular compound 5 is 2.0×10^{-3} .

Weight average molecular weight was 3.4x10 4.

[0232]

Example 7

<Composition of the high molecular compound 6>

Compound E 400 mg, 2,3-diethyl- 5,8-dibromoquinoxaline 97 mg and 2, 2'-bipyridyl After teaching 300 mg to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 20 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 460 mg of bis(1,5-cyclo-octadiene) nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 50 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene derivative and a quinoxaline derivative is 70:30.

This copolymer is called the high molecular compound 6.

The number average molecular weight of polystyrene conversion of the high molecular compound $6 ext{ is } 2.5 ext{x} 10^{-4}$.

The polystyrene equivalent weight average molecular weight was 9.0x10 4.

[0233]

Example 8

Composition of the high molecular compound 7>

Compound E 350 mg, N, N'-screw (4-bromophenyl) - N, The N'-screw (4-n-buthylphenyl) 1, 57 mg of 4-phenylenediamines (amine derivative 1), N,N-bis(4-bromophenyl)-N-(4-(1-methylbutyl) phenyl) amine (amine derivative 2) 78 mg and 2, 2'-bipyridyl After teaching 330 mg to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 24 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 600 mg of bis(1,5-cyclo-octadiene)nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 76 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene derivative, the amine derivative 1, and the amine derivative 2 is 70:10:20.

This copolymer is called the high molecular compound 7.

The number average molecular weight of polystyrene conversion of the high molecular compound 7 is 7.4×10^{-4} .

Weight average molecular weight was 2.4x10 5.

[0234]

Example 9

Composition of the high molecular compound 8>

Compound E 310 mg and N,N'-screw (4-bromophenyl) - N, N'-(4-buthylphenyl)-1,4phenylenediamine 310 mg, Bis(4-bromophenyl)ether 170 mg and 2,2'-bipyridyl 500 mg is put into a flask, In the bottom of the nitrogen atmosphere after dissolving in drying tetrahydrofuran 70mL beforehand deaerated with argon gas after carrying out the nitrogen purge of the inside of a system, To this solution, it is bis(1, 5-cyclo-octadiene)nickel (0) {nickel(COD) 2}. Temperature up was carried out and it was made to react to 60 ** in addition for 3 hours 910 mg. This reaction mixture is cooled to a room temperature after a reaction, and after filling reaction mixture with 20 ml of 100 ml of 20 ml of 25% ammonia solutions / methanol / ion exchange water and stirring it for 1 hour, reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 40 ml of toluene. The water layer was removed, after adding 1N chloride 40mL, stirring for 1 hour, having removed the water layer, adding ammonia solution 40mL to the organic layer 3% and stirring for 1 hour. The organic layer which 30 ml of ion exchange water furthermore washed, and was washed to methanol 100mL was poured out, and it stirred for 1 hour. Reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in toluene 40mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 200mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 130 mg. In a copolymer, the ratio of the repeating unit corresponding to a dibenzo thiophene derivative, an amine derivative, and diphenyl ether is 35:30:35.

This copolymer is called the high molecular compound 8. The number average molecular weight of polystyrene conversion of the high molecular compound 8 was Mn= 7.4×10^{-3} , and weight average molecular weight was Mw= 1.4×10^{-4} . [0235]

Example 10 (composition of compound F)

Compound F

According to the procedure which compounded E, it compounded from compound A. 46% of yield, 96% of purity.

 1 H-NMR (300 MHz/CDCl $_{3}$):

delta 0.89 (dd, 12H), 1.01 (d, 6H), 1.17-2.01(m, 20H)4.18 (t, 4H), 7.42 (s, 2H), 7.92 (s, 2H) MS (APCI (+)) -- according to the law, the peak was detected by 671 and 654. [0236]

Example 11

Composition of the high molecular compound 9>

Compound F 1000 mg and 2,2'-bipyridyl In the bottom of the nitrogen atmosphere after dissolving in drying tetrahydrofuran 60mL beforehand deaerated with argon gas after putting 830 mg into the flask and carrying out the nitrogen purge of the inside of a system, To this solution, it is bis(1, 5-cyclo-octadiene)nickel (0) {nickel(COD) }_2}. Temperature up was carried out and it was made to react to 60 ** in addition for 3 hours 1500 mg. This reaction mixture is cooled to a room temperature after a reaction, and after filling reaction mixture with 150 ml of 75 ml of 15 ml of 25% ammonia solutions / methanol / ion exchange water and stirring it for 1 hour, reduced

pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 40 ml of toluene. The water layer was removed, after adding 1N chloride 40mL, stirring for 1 hour, having removed the water layer, adding ammonia solution 40mL to the organic layer 3% and stirring for 1 hour. The organic layer which 60 ml of ion exchange water furthermore washed, and was washed to methanol 100mL was poured out, and it stirred for 1 hour. Reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in toluene 40mL. Then, it refined through the alumina column (the amount of alumina of 10g), the collected toluene solution was dropped at methanol 200mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained polymer was 100 mg. This polymer is called the high molecular compound 9.

The number average molecular weight of polystyrene conversion of the high molecular compound 9 was Mn= 5.0×10^{-4} , and weight average molecular weight was Mw= 1.1×10^{-5} . [0237]

Example 12

Composition of the high molecular compound 10>

Compound F 320 mg, compound E After teaching 310 mg and 2, and 340 mg of 2'-bipyridyls to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 24 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 600 mg of bis(1,5-cyclo-octadiene)nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 300 mg. In a copolymer, the ratio of the repeating unit corresponding to compound F and compound E is 50:50. This copolymer is called the high molecular compound 10.

The number average molecular weight of polystyrene conversion of the high molecular compound 10 is 8.8×10^{-4} .

Weight average molecular weight was 3.0x10 5.

[0238]

Example 13

Composition of the high molecular compound 11>

Compound F 320-mg, N, and N'-screw (4-bromophenyl) – After teaching N, the N'-screw (4-n-buthylphenyl) 1, 140 mg of 4-phenylenediamines, and 2 and 310 mg of 2'-bipyridyls to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 22 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 550 mg of bis(1,5-cyclo-octadiene)nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia

solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 150 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene derivative and an amine derivative is 70:30.

This copolymer is called the high molecular compound 11.

The number average molecular weight of polystyrene conversion of the high molecular compound 11 is $3.9x10^{-3}$.

Weight average molecular weight was 4.4x10 4.

[0239]

Example 14

Composition of the high molecular compound 12>

Compound F 270 mg, compound E 250 mg, N, N'-screw (4-bromophenyl) - N, After teaching the N'-screw (4-n-buthylphenyl) 1, 240 mg of 4-phenylenediamines and 2, and 400 mg of 2'bipyridyls to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 28 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 700 mg of bis(1,5-cyclo-octadiene) nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 190 mg. In a copolymer, the ratio of the repeating unit corresponding to compound F, compound E, and an amine derivative is 35:35:30. This copolymer is called the high molecular compound 12.

The number average molecular weight of polystyrene conversion of the high molecular compound 12 is 3.8×10^{-4} .

Weight average molecular weight was 5.9x10 4.

[0240]

example 15 (composition of the compound G)

Compound G

E was compounded according to the procedure which carries out synthetic composition from compound A. 53% of yield, 100% of purity.

¹H-NMR (300 MHz/CDCl₃):

delta 1.00 (d, 12H), 1.75 (dd, 2H), 1.87(m, 4H)4.11 (t, 4H), 7.07 (dd, 2H), 7.55 (d, 2H), 7.68 (s, 2H) [0241]

Example 16

⟨Composition of the high molecular compound 13⟩

Compound G 260mg, compound E After teaching 300 mg and 2, and 310 mg of 2'-bipyridyls to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. Bubbling was beforehand carried out to this with argon gas, and 22 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 550 mg of bis(1,5-cyclo-octadiene)nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 150 mg. In a copolymer, the ratio of the repeating unit corresponding to the compound G and compound E is 50:50.

This copolymer is called the high molecular compound 13.

The number average molecular weight of polystyrene conversion of the high molecular compound $13 \text{ is } 9.0 \times 10^{-4}$.

Weight average molecular weight was 2.0x10 5.

[0242]

Example 17

Composition of the high molecular compound 14>

Compound E After teaching the 300-mg, compound G 64mg, N, and N'N, N'-screw (4-nbuthylphenyl) 1, 180 mg of 4-phenylenediamines and 2, and 280 mg of 2'-bipyridyls to a reaction vessel, nitrogen gas replaced the inside of the system of reaction. [- screw (4-bromophenyl) -] Bubbling was beforehand carried out to this with argon gas, and 20 ml of deaerated tetrahydrofurans (dehydration solvent) were added. Next, 500 mg of bis(1,5-cyclo-octadiene) nickel (0) was added to this mixed solution, and it reacted to it at 60 ** for 3 hours. The reaction was performed in a nitrogen gas atmosphere. After the reaction, after cooling this solution, it poured into 120 ml of 10 ml of 25% ammonia solutions / methanol / 50 ml of ion-exchange-water mixed solution, and stirred for about 1 hour. Next, the generated precipitate was collected by filtering. After washing this precipitate by ethanol, reduced pressure drying was carried out for 2 hours. Next, it stirred for 1 hour, this precipitate was dissolved in toluene 30mL, 1N chloride 30mL is added, ammonia solution 30mL was added [the water layer removed,] to the organic layer 4%, and the water layer was removed after stirring for 1 hour. The organic layer was dropped at methanol 150mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 30mL. Then, it refined through the alumina column (the amount of alumina of 20g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 80 mg. In a copolymer, the ratio of the repeating unit corresponding

to the compound G, compound E, and an amine derivative is 56:14:30.

This copolymer is called the high molecular compound 14.

The number average molecular weight of polystyrene conversion of the high molecular compound 14 is 3.2×10^{-4} .

Weight average molecular weight was 6.3x10 4.

[0243]

synthetic example 18 (composition of the compound H)

Compound H

Under an inert atmosphere, it is compound E. It is dichloromethane about 1.0 g. After melting in 11 ml and dissolving thoroughly, 3.5 ml of boron tribromide (1.0 mol/l dichloromethane solution) was dropped. It warmed at 40 ** after the end of dropping, and agitated for 5 hours. 0 ** of ion exchange water was filled with reaction mixture, and it agitated for 1 hour. The depositing solid was filtered and 0.60 g of objects were obtained by carrying out vacuum drying (96% of yield, 99% of purity).

 1 H-NMR (300 MHz / (CD₃) ₂SO) :

delta 7.60 (s, 2H), 8.16 (s, 2H), 10.485 (br, 2H)

MS(APCI (-)): (M-H)-373

[0244]

Example 19 (composition of the compound J)

Compound J

a reaction vessel — the compound H — 5.00g and 1 — 11.4 g of bromination (4— pentylphenoxypropane), and potassium carbonate 9.24 g and DMF 75ml were put in, and heating flowing back was carried out for 4.5 hours. Toluene and water separated, the organic layer was extracted and it dried with sodium sulfate. The flash column was performed with toluene after removing a solvent, and 7.77 g of objects were obtained by carrying out heating washing twice by hexane. 74% of yield. 100% of purity.

 1 H-NMR (300 MHz/CDCl₃):

delta 0.88 (t, 6H), 1.24-2.55 (m, 20H), 4.25 (t, 4H), 4.34 (t, 4H), 6.86 (dd, 4H), 7.07 (dd, 4H), 7.49 (s, 2H), 7.94 (s, 2H)

[0245]

Example 20

Composition of the high molecular compound 15>

Compound J 391mg and 2,2'-bipyridyl In the bottom of the nitrogen atmosphere after dissolving in tetrahydrofuran 14mL which dried 130 mg, To this solution, it is bis(1, 5-cyclo-octadiene) nickel (0) $\{\text{nickel(COD)}_2\}$. Temperature up was carried out and it was made to react to 60 ** in

addition for 3 hours 230 mg. After cooling this reaction mixture to a room temperature after a reaction, being dropped into 80 ml of 7 ml of 25% ammonia solutions / methanol / 40 ml of ion-exchange-water mixed solution and stirring for 1 hour, reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 20 ml of toluene. The water layer was removed, after adding 1N chloride 20mL, stirring for 3 hours, having removed the water layer, adding ammonia solution 20mL to the organic layer 4% and stirring for 3 hours. The organic layer was dropped at methanol 100mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was made to dissolve it in toluene 20mL. Then, it refined through the alumina column (the amount of alumina of 10g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained polymer was 220 mg.

This polymer is called the high molecular compound 15.

The number average molecular weight of polystyrene conversion of the high molecular compound 15 was Mn=2.3x10⁻⁵, and weight average molecular weight was Mw=1.1x10⁻⁶. [0246]

Example 21

Composition of the high molecular compound 16>

Compound J 274mg and N,N'-bis(4-bromophenyl)-N,N'-bis(4-n-buthylphenyl)-1,4-phenylenediamine 102 mg and 2,2'-bipyridyl After dissolving in tetrahydrofuran 14mL which dried 160 mg, In the bottom of a nitrogen atmosphere, it is bis(1, 5-cyclo-octadiene)nickel (0) {nickel (COD) } to this solution. Temperature up was carried out and it was made to react to 60 ** in addition for 3 hours 290 mg. After cooling this reaction mixture to a room temperature after a reaction, being dropped into 80 ml of 7 ml of 25% ammonia solutions / methanol / 40 ml of ion-exchange-water mixed solution and stirring for 1 hour, reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours, and it was made to dissolve in 20 ml of toluene. The water layer was removed, after adding 1N chloride 20mL, stirring for 3 hours, having removed the water layer, adding ammonia solution 20mL to the organic layer 4% and stirring for 3 hours. The organic layer was dropped at methanol 100mL, was stirred for 1 hour, filtered and carried out reduced pressure drying of the precipitate which deposited for 2 hours, and was

made to dissolve it in toluene 20mL. Then, it refined through the alumina column (the amount of alumina of 10g), the collected toluene solution was dropped at methanol 100mL, it stirred for 1 hour, and reduced pressure drying of the precipitate which deposited was filtered and carried out for 2 hours. The yield of the obtained copolymer was 50 mg. In a copolymer, the ratio of the repeating unit of a dibenzo thiophene derivative and an amine derivative is 70:30.

This copolymer is called the high molecular compound 16.

The number average molecular weight of polystyrene conversion of the high molecular compound 16 was Mn=8.1x10 ⁴, and weight average molecular weight was Mw=5.6x10 ⁵. [0247]

Example 22

<Fluorescent characteristic>

The spin coat of the 0.2wt% chloroform fluid of the high molecular compounds 1–18 was carried out on quartz, and the thin film of the high molecular compound was produced, respectively. The fluorescence spectrum of these thin films was measured using the spectrophotofluorometer (Hitachi 850). All have strong fluorescence and showed the fluorescence peak wavelength and fluorescence intensity which are shown in following Table 1, respectively. [0248]

[Table 1]

高分子化合物	蛍光ピーク(nm)	蛍光強度
1	426	0.67
2	474	1.65
3	470	1.62
4	450	4.13
5	440	1.82
6	458	3.96
7	468	2.89
8	461	2.14
9	472	1.73
10	438	1.76
11	480	2.18
12	474	3.32
13		
	418	1.38
14	476	2.92
15	403	1.94
16	469	3.37

[0249]

Example 23

<Element characteristic>

To the glass substrate which attached the ITO film by a thickness of 150 nm by the sputtering technique. Membranes were formed by a thickness of 50 nm with the spin coat using the solution (a Beyer company, BaytronP) of poly (ethylene dioxythiophene)/polystyrene sulfonate, and it dried for 10 minutes at 200 ** on the hot plate. Next, membranes were formed with the revolving speed of 800 rpm with the spin coat using the toluene solution which prepared the various high molecular compounds obtained above so that it might become 1.5wt%. Thickness was about 60 nm. After drying this at 80 ** under decompression for 1 hour, calcium was vapor-deposited for LiF as a cathode buffer layer, subsequently about 5 nm of aluminum [about 80 nm of] was vapor-deposited as about 4 nm and the negative pole, and the EL element was produced. The degree of vacuum started metaled vacuum evaporation, after reaching below 1x10⁻⁴Pa. By **** (ing) voltage for the obtained element, the EL luminescence and the highest EL luminescence efficiency which are shown in the following table 2 were obtained from these elements. The intensity of EL luminescence was proportional to current density mostly. [0250]

[Table 2]

高分子化合物	ELピーク(nm)	発光効率(cd/A)
2	480	0.12
4	452	0.55
5	428	0.02
6	472	0.03
7	460	0.07
9	460	0.36
10	412	0.31
11	492	0.37
12	472	0.60
13	436	0.37
14	468	0.28
15	428	0.50
16	480	1.85

[0251]

Example 40

<Manufacture of the high molecular compound 23>

High molecular compound 13 2mg, Ir complex Btp₂Ir (acac) 0.1mg was dissolved in 0.2 ml of toluene, and membranes were formed by a thickness of about 200 nm with the spin coat. One evening of this was dried at the bottom room temperature of decompression. When the fluorescence spectrum of the obtained thin film was measured, phosphorescence luminescence from Ir complex was observed.

[0252]

[Effect of the Invention]

The high molecular compound which has a thiophene condensed ring unit of this invention is a new high molecular compound usable as a luminescent material, a charge transporting material, etc. These polymers and the ink composition containing it can be used as materials, such as a polymers light emitting device, an organic electroluminescence device which used it, and an organic FET device.

[Translation done.]